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Baltic Slurry Acidification

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Working environment and safety

Report from WP2, Activity 5

Kikki Fors, Niklas Adolfsson, Hanna Bannbers, Lena Rodhe, Line Strand, Erik Sindhöj, Henning L. Foged, Kalvi Tamm, Sari Peltonen, Sebastian Neumann, Jānis Kažotnieks, Artūras Šiukščius, Witold Wardal, Marcin Majchrzak

EU STRATEGY FOR THE BALTIC SEA REGION
FLAGSHIP

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Preface

Baltic Slurry Acidification is a flagship project in the action plan for EU strategy for the Baltic Sea Region (BSR). The project is being carried out between 2016-2019 with a budget of 5.2 million euros, of which 4 million euros is funded by the EU Regional Development Fund through the Interreg Baltic Sea Region Programme.

The general aims of the project are to reduce ammonia emissions from animal production and create a more competitive and sustainable farming sector by promoting the implementation of slurry acidification techniques (SATs) throughout the Baltic Sea Region. This report falls under Work Package 2, Activity 5 – Working environment and safety.

This report presents a general overview of safety needs for handling acids and relevant EU-legalisations. Additionally, there are country specific regulations and conditions for implementation and use of slurry acidification technologies. All eight countries involved in the project are represented by chapters, which includes several authors. In chapter '*Contact information to authors, country wise*' are the contact information given for all authors.

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Erik Sindhöj
Project Coordinator for Baltic Slurry Acidification

Summary

This report concerns working environment and safety when implementing technologies for acidification of animal slurry in the Baltic Sea Region. Ammonia is volatilised from manure when it is managed in livestock housing and during storage and when it is applied to fields, and the ammonia will contribute to eutrophication of the Baltic Sea. Slurry acidification is a known technology to reduce ammonia emissions from manure in livestock housing, during storage and during and after application in fields. Acidification technologies have been developed in Denmark, where approximately 18% of all slurry was acidified in 2014. So far, it is not practised generally in the Baltic Sea Region, largely because the technology is not available and because of a general lack of experience. One other concern is the working environment and safety when handling such dangerous chemical, which can cause severe chemical burns to skin and eyes and other health problems.

This report starts with a general overview of properties of acids with particular focus on sulphuric acid since it is the most common acid used in acidification technologies. There are several EU regulations governing the sale of chemicals including specific requirements for hazard classifications and labelling. The REACH Regulation covers the registration, evaluation, authorization and restriction of chemicals. REACH also imposes requirements on the users of chemicals, termed downstream users. The CLP Regulation relates to the classification, labelling and packaging of chemical substances and mixtures placed on the market within the EU. For occupational safety and health and work environment there are many regulations to follow as well as personal protective equipment to use.

For each of the Baltic Sea Region countries, there are presentations of national regulations and general aspects on working environment, personal safety, safe storage and transport. Also, there are example scenarios of how to handle the acid in order to prevent accidents when using slurry acidification technologies suitable for the slurry handling systems in each country.

The below recommendations were compiled in the project group to be used if implementing slurry acidification technology on farm level:

- Find a safety advisor.
- Make a risk analysis.
- Chose the safest technology (no or little risk of contact acid handling).
- Get training.
- Follow maintenance program from supplier.
- Use protection equipment.
- Be prepared for accidents and know what to do.

Introduction

Manure from housing in livestock production is a source of nitrogen input to the Baltic Sea in the form of leakage to water and atmospheric emissions. Ammonia is volatilised from manure when it is managed in livestock housing and during storage and application. Agriculture accounts for the largest share of ammonia emissions. Measures to reduce ammonia emissions from agriculture therefore have a major impact on total emissions. Reducing the leaching of nitrogen from agriculture plays an important part in reducing the eutrophication of the Baltic Sea. Reducing nitrogen losses from manure from livestock housing also increases the supply of nutrients to crops under cultivation and the efficiency of nitrogen recycling. Manure from livestock housing with a higher nutrient value results in better developed crops. These can take up more phosphorus, which imposes an environmental load, compared with less well developed crops. Reducing nitrogen losses by improving the management of manure from livestock housing therefore offers many benefits for the environment and the grower.

Slurry acidification is known to be a way of reducing ammonia emissions from manure in livestock housing, during storage and during and after application in fields (Petersen, 2012). It is not practised in Sweden, however, largely because the technology is not available and because of a general lack of experience. Acidification technology is currently being developed in Denmark, where 18% of all slurry was acidified in 2014 (SEGES, 2015). Acidification reduces losses of nitrogen by shifting the chemical equilibrium between ammonium and ammonia towards a higher proportion of ammonium nitrogen, which cannot be emitted in gaseous form.

Technology is available for acidification in livestock housing and during storage and application. The aim in livestock housing and storage is for the pH of the manure to be less than 5.5 so the effect persists for longer, i.e. during subsequent storage and application. In testing using the VERA test protocol, ammonia emissions were reduced by 64% from stables by using acidification in pig stables with technology from the JH Agro A/S (ETA-Denmark, 2011). In one of the two stables, it was also shown an odour reduction of 29% on yearly basis. Acidification in livestock housing is not actually employed in Sweden, given the current system and legislation. A system for adding acid while the manure is in storage may be suitable instead. Here, the aim is to have the pH <6 if the acid is added before application. To limit the quantity of acid required, it is important to start application as soon as possible after the sulphuric acid is mixed with the manure in the storage facility, because of the manure's buffering capacity, which cause the pH to rise. To acidify slurry during application, it is dosed with sulphuric acid automatically during field operations using one of the various technologies available on the market. The objective is to reach the manure pH <6.4 during application according to Danish regulations to be approved as an ammonia-limiting measure and an alternative to incorporating the manure into the soil during application. In tests according to VERA, the reduction of ammonia was 49% when applied cattle slurry VERA, 2012). No effect on odour emission reduction efficiency could be shown.

General information about acids and basis

Acids, bases, salts, gases, enzymes, fertilizers, oils and lubricants, pharmaceuticals, detergents, etc., are all chemicals used by humans. They can be corrosive, odorous, harmful to human health and/or toxic. Examples of acids are sulphuric acid (pH <0), formic acid, hydrochloric acid, hydrofluoric acid (which can dissolve glass) and acetylsalicylic acid. Examples of bases are ammonia, quicklime (calcium oxide) and caustic soda (pH 14). Acids are characterized by providing hydrogen ions (H^+) in solution, while bases provide hydroxide ions (OH^-). The acidity of acids and bases is measured in pH, with values between 0 and 14. Low pH means acidic (acids) and high pH means basic (alkalis). The value pH 7 is neutral, corresponding to pure, distilled water. pH can only be measured with the substance in solution, i.e. in terms of the concentration of hydrogen ions (H^+). The pH scale is negative logarithmic. Dilution by a factor of ten changes the pH by one unit.

pH 1 =10^{-1} = 1/10

pH 7 = 10^{-7} =1/10 000 000

pH 14 = 10^{-14} = 1/ 100 000 000 000 000

For example, a lake with pH 5 is ten times more acidic than one with pH 6, and a hundred times more acidic than one with pH 7. Diluting a discharge of 10 litres of an acid with pH 3 to a value close to pH 7 theoretically requires ten tankers of the volume 10 m^3.

Both acids and bases are more or less corrosive, but in different ways. Acids are hygroscopic and take up water in contact with carbohydrates, which is why acids cause burn injuries to skin. Bases, on the other hand, dissolve fats and proteins, causing corrosion injuries.

Sulphuric acid is one of the chemical industry's most important base chemicals. It is used in the production of other acids (e.g. hydrochloric acid), in the manufacture of fertilizers and explosives and in the processing of crude oil into various petroleum products.

Why sulphuric acid?

Sulphuric acid is not only the most suitable acid for acidifying slurry, but also the most cost-effective. Furthermore, it supplies sulphur, which is a macronutrient that plants need. Hydrochloric acid (HCl) forms chloride ions that are very corrosive to all materials, e.g. in a concrete tank. The acid corrodes iron. Nitric acid (HNO_3) reacts with organic material and releases nitrogen to the air. Phosphoric acid (H_2PO_3) contains phosphorus, and therefore contributes to more phosphorus going onto fields and to eutrophication if not deficit in soil. Weaker acids are not suitable, either, because they require unmanageably large volumes to acidify the manure.

Sulphuric acid properties

Pure sulphuric acid is a strong, colourless, viscous and odourless acid, with pH <0. It has a high density (1.84 g/cm^3). The melting/freezing point is -11 °C, and the boiling point approx. 330 °C. Sulphuric acid has dehydrating properties because it absorbs moisture and water from its surroundings. Its pK_a value is ≈-31[1]. Sulphuric acid is classified as a substance with pH ≤ 2 that is highly corrosive to skin and eyes. It damages the eyes irreversibly. It is so powerful that it leaves behind only carbon from organic materials such as paper. Skin is very quickly damaged in the same way. The acid reacts vigorously with water, generating heat that causes boiling and violent splashing. These splashes can cause more damage to tissue than the strength of the acid might suggest. It is therefore absolutely vital to use the right extinguishing agent in the event of a fire where sulphuric acid is stored. Do not use water. Use foam, dry powder, carbon dioxide or dry sand.

Sulphuric acid vapours can also be harmful to the respiratory tract and mucous membranes. Sulphuric acid is also classified as a CMR substance[2], and is carcinogenic when inhaled as an aerosol. Exposure to CMR substances must always be limited as far as is reasonably possible. Some CMR substances have occupational exposure limit values. Exposure below the limit value is considered safe. In most cases, CMR substances are dangerous if the substance is inhaled, ingested or absorbed through the skin. It is therefore important to consider the whole management chain, including equipment cleaning and waste management. It is also important to remember not to spread the substance via contaminated gloves, clothing, etc. The risk assessment should therefore result in the adoption of strict risk-limitation measures. It is vital that the employees concerned are informed about them. Written handling and safety instructions must always be available.

The correct personal protective equipment is therefore imperative when sulphuric acid is handled. For this reason, employers and others concerned are subject to clear undertakings.

AIW, Acid Into Water

Mixing a strong acid with water is a exoterm reaction and if water is poured into acid the result will be boiling and splashing acid. This can cause severe chemical burns to skin and eyes. Therefore, the acid should always be poured into water (AIW) in small proportions with stirring, in order to control the heat development. So, Acid Into Water is a memory rule in chemistry which tells that strong acids should be diluted by poured into water, not the opposite!

[1] An acid dissociation constant (K_a or K_s) is a specific type of equilibrium constant that indicates the extent to which an acid can be protonated, i.e. the proportion of the acid that reacts with water to form hydronium ions (H_3O^+) in aqueous solution. Wikipedia 2016-10-28.

[2]Substances that are carcinogenic, mutagenic or toxic to reproduction, according to Annex VI of the CLP Regulation.

Properties of Sulphuric Acid in slurry

The sulphuric acid must be poured into the slurry tank in accordance with the acid-into-water (AIW) rule (see heading above). It has a high density (1.84 g/cm^3). The acid should be added with stirring to prevent it forming a layer at the bottom. The sulphuric acid reacts with the proteins in the slurry, generating carbon dioxide that leads to extensive foaming. It is therefore important that there is enough space in the tank to prevent the foam overflowing when the acid is added. Antifoaming agents can be used. Otherwise, the foam eventually subsides, but this can take some time.

EU-legislation of chemicals

In addition to national regulations, there are EU regulations governing the sale of chemicals on the market and hazard classification and labelling. The REACH Regulation covers the registration, evaluation, authorization and restriction of chemicals. REACH also imposes requirements on the users of chemicals, termed downstream users. The CLP Regulation relates to the classification, labelling and packaging of chemical substances and mixtures placed on the market within the EU.

REACH Regulation
Regulation (EC) No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

The purpose of REACH is to ensure a high level of protection of human health and the environment. It shall apply without prejudice to Community workplace and environmental legislation.

CLP regulation
Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing. Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.CLP.

The objective of this Regulation (CLP) should be to determine which properties of substances and mixtures should lead to a classification as hazardous, in order for the hazards of substances and mixtures to be properly identified and communicated. Such properties should include physical hazards as well as hazards to human health and to the environment, including hazards to the ozone layer.

Whereas Article 118a of the Treaty provides that the Council shall adopt by means of Directives minimum requirements for encouraging improvements, especially in the working environment, to guarantee a better level of protection of the safety and health of workers.

Council directive 98/24/EC of 7 April 1998on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)

Another Directive has as its aim the protection of workers against risks to their health and safety, including the prevention of such risks, arising or likely to arise from exposure to carcinogens or mutagens at work. It lays down particular minimum requirements in this area, including limit values.

Directive 2004/37/EC of the European Parliament and of the Council of 29 April 2004on the protection of workers from the risks related to exposure to carcinogens or mutagens at work (Sixth individual Directive within the meaning of Article 16(1) of Council Directive 89/391/EEC)

Labelling and classification

Since 1 June 2015, labelling must comply with the CLP Regulation. CLP[3] stands for the classification, labelling and packaging of chemical substances and mixtures. It applies to all chemical substances delivered or supplied within the EU. Mixtures in packaging labelled in accordance with the earlier regulations, imported or sold before that date, may retain the old labelling. From 1 June 2017, they must all have the new labelling in accordance with CLP.

Hazard pictograms

Signal words
Danger

Hazard class
Skin corrosion, Category 1A - H314
Dangerous to the aquatic environment, acute, Category 1 - H400

Hazard statements
H314 – Causes severe skin burns and eye damage
H400 – Very toxic to aquatic life

[3] Classification, Labelling and Packaging of substances and mixtures.

Personal safety

Is permission required?

In accordance with Annex XIV of REACH, a permit is required to use or place certain particularly dangerous substances on the market. This applies regardless of the quantity of these substances handled. It does not apply to sulphuric acid, however. It is important to know that sulphuric acid must not be used for professional purposes by young people under 18 years.

EU legislation on occupational safety and health and work environment responsibilities

Occupational safety and health and work environment responsibilities are regulated by EU and national legislation. The legislation covers requirements concerning exposure limit values, protective measures and risk assessments in different directives.

Council directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC).

This Directive, which is the fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC, lays down minimum requirements for the protection of workers from risks to their safety and health arising, or likely to arise, from the effects of chemical agents that are present at the workplace or as a result of any work activity involving chemical agents.

Directive 2004/37/EC of the European Parliament and of the Council of 29 April 2004 on the protection of workers from the risks related to exposure to carcinogens or mutagens at work (Sixth individual Directive within the meaning of Article 16(1) of Council Directive 89/391/EEC).

Compliance with the minimum requirements designed to guarantee a better standard of health and safety as regards the protection of workers from the risks related to exposure to carcinogens or mutagens at work is essential to ensure the health and safety of workers and is also intended to provide a level of minimum protection for all workers in the Community.

Commission Directive 2006/15/EC of 7 February 2006 establishing a second list of indicative occupational exposure limit values in implementation of Council Directive 98/24/EC and amending Directives 91/322/EEC and 2000/39/EC.

For any chemical agent for which indicative occupational exposure limit values are established at Community level, Member States are required to establish a national occupational exposure limit value taking into account the Community limit value, but may determine its nature in accordance with national legislation and practice.

Protective equipment

Personal protective equipment is regulated in EU-directive (89/686/EEG).

Council Directive 89/686/EEC of 21 December 1989 on the approximation of the laws of the Member States relating to personal protective equipment.

This Directive applies to personal protective equipment, hereinafter referred to as 'PPE'. It lays down the conditions governing its placing on the market and free movement within the Community and the basic safety requirements which PPE must satisfy in order to ensure the health protection and safety of users.

All protective equipment used must be CE-marked. For protective clothing to be CE-marked[4], it must be tested by an accredited testing institute and certified by a notified body, and the product or production must be subject to production control. Appropriate personal protective equipment is acid-resistant safety boots/shoes; fully covering acid-resistant protective suit (e.g. in butyl rubber or neoprene), which may be disposable; protective gloves (in fluorocarbon rubber 0.4 mm thick or butyl rubber 0.5 mm thick) certified in accordance with EN 374-2003 (fabric, leather, natural rubber, polychloroprene/chloroprene rubber and nitrile rubber are unsuitable materials); and protective eyewear or a full-face mask at concentrations above the occupational exposure limits (with gas filter E, release of sulphur dioxide, or an aerosol mask with filter P3, mist formation) in accordance with SS-EN 141. See Figure 1 and 2.

Fig. 1. CE-marked chemical protection gloves in neoprene[5] (0.75 mm thick), certified in accordance with EN 374.

[4] Certification enables the manufacturer to CE-mark the product, which is a necessity for being able to place the product on the European market. Directive 89/686/EEC, sometimes called the PPE Directive (Personal Protective Equipment)

[5] www.skydda.com

Fig. 2. Experimental staff wearing personal protective equipment while handling sulphuric acid.

Storage

For safety reasons, acids must be stored in the dry and at room temperature[6]. It must be kept separate from heat sources, combustible materials, metals, organic materials, etc. In contact with these, the acid can cause fire, explosion (formation of hydrogen gas with metals) or self-ignition (organic materials). It must be stored in acid-resistant original containers in a well-ventilated area, and located safely[7].

Corrosive substances (acids, caustic solutions) often require plastic (polyethene) bunding. Sulphuric acid with a concentration of 95% is often stored in stainless steel containers, which have to be of a type of stainless steel corresponding to EN 1.4301[8]. If the concentration is 78% or less, it can also be stored in plastic (polyethene) containers. Figure 3 is shown as a terrible warning!

Sulphuric acid must not be stored above eye level.

[6] The melting/freezing point of sulphuric acid is -11 °C.
[7] Located safely means the container is positioned sufficiently low to prevent getting the chemical in the face when drawing it off.
[8] EN 1.4301 is an austenitic (gamma iron) stainless steel with good resistance to corrosion and high temperatures. It is far superior to ferritic (chromium steel) stainless steel in most applications and environments.

Fig. 3. How not to handle sulphuric acid. Sulphuric acid must not be handled or stored above eye level.http://www.harso.dk/sikkerhed-syre.html

The packaging must be tightly closed because the acid is hygroscopic and becomes unstable when damp. Packaging means drums, barrels, IBCs[9], etc. Tanks and tank containers are not regarded as packaging. Suitable storage materials are cast iron, PTFE-lined steel, carbon steel and PTFE (polytetrafluoroethene, fluorinated plastic such as Teflon and Gore-Tex, for example). The acid can be corrosive to metals (Hazard statement H290), so containers in Monel[10], lead, aluminium, iron, copper, zinc, etc., should be avoided. With most of these metals, the acid generates hydrogen gas (also called oxyhydrogen gas), which is explosive.

Containers used or stored in connection with use must be labelled in accordance with CLP (name, hazard pictograms and text, in this case "Corrosive", and information about the product's carcinogenicity). This also applies to any visible pipework, which must also have an arrow indicating the direction of flow. The storage site may require bunding and protection against collision to prevent the risk of accidents and to prevent contamination of ground-, waste- and surface water.
The capacity of the bunded area is usually the total volume of the largest container plus 10% of that of other containers. The material must be suitable for sulphuric acid. Any pipework involved must be double containment pipework. See examples in the Figure 4 for indoor and outdoor storage.

[9]IBC:Intermediate Bulk Containers are large containers with a maximum volume of 3 m^3.
[10] Monel is an alloy consisting of 65-70% nickel, 20-29% copper, 2-5% manganese, traces of iron, aluminium, silicon, titanium and sulphur. Wikipedia 2016-10-28.

Fig. 4. Secure storage indoors[11] (space for three IBCs) and outdoors (space for one IBC) with sump for IBCs, etc. Corrosion-resistant, strong, rigid construction in environmentally friendly PE plastic (polyethene) and PE grid. Those for outdoor use are weather-resistant with roller doors[12] or a door like the blue environmental container[13].

If sulphuric acid is to be stored in winter, it is important to know the storage temperatures in accordance with the safety data sheets. Boliden's safety data sheet for 96% sulphuric acid states that the acid must be stored in a dry location at room temperature.

Measures are sometimes required to prevent and limit the consequences of serious chemical accidents that, as a result of uncontrolled events, may cause serious danger to human health or the environment within or outside the activity. Sulphuric acid is not mentioned in Annex 1 of the Seveso Directive[14].

Companies that market equipment for adding acid to slurry supply acid tanks, for example for fixed installation (Fig. 5) or for front-mounting on tractors (Fig. 6).

[11] http://www.denios.com 2016-11-01.
[12] www.pk-produkter.se. 2016-11-01.
[13] http://www.denios.com 2016-11-01.
[14] Act (1999:381) and Ordinance (2015:236) on measures to prevent and limit the consequences of serious chemical accidents (Seveso).

Fig. 5. Fixed acid tank surrounded by protective bollards, and with shower (JH Agro A/S).

Fig. 6. Mobile intermediate bulk container (IBC) in frame, open (left) and enclosed (right) (made by BioCover A/S).

Environment

Nature has also to be protected from pollutions from acid. There are legalisations on EU-level to prevent pollution.

Directive 2004/35/CE of the European parliament and of the council of 21 April 2004 on environmental liability with regard to the prevention and remedying of environmental damage.

Art 1. The purpose of this Directive is to establish a framework of environmental liability based on the 'polluter-pays' principle, to prevent and remedy environmental damage.

The overall objective of both EU and national environment laws is to protect human health and the environment against damage and disturbance whether caused by pollution or some other effect. Applying this to the handling of the sulphuric acid means discharges to waste-, ground- and surface water must be prevented. Spillages are confined and absorbed, using absorbent material, sand, diatomaceous earth or similar, and collected. Sawdust, bark or similar materials must not be used because of the risk of fire. The contaminated area is sluiced with water. Major spillages are dammed in suitable receptacles, and the emergency services are contacted. If necessary, buffering lime or sodium carbonate is applied. It is important to have

buffering material available during handling. Waste from the clean-up is dealt with as dangerous waste. Major discharges to the wastewater system may harm the wastewater treatment plant by inhibition of the sludge or biofilm organisms due to acidification.

Waste

Handling of waste like old tanks and small rests of acid must be made in a safe way. It is regulated in EU-legalisation and national laws. Dirty tanks should also be handled as dangerous waste.

Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.

The directive defines key concepts such as waste, recovery and disposal and puts in place the essential requirements for the management of waste.

Commission decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous waste pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.

The decision establishes what is hazardous waste. Waste containing sulphuric acid is considered hazardous.

Waste classification

Sulphuric acid residues (more than 1% of the container volume) are considered dangerous waste and must be handled accordingly. Waste codes are listed in the European Waste Catalogue (EWC).

Fire

Sulphuric acid itself is not a combustible material. In the event of a major fire with high temperatures, however, sulphuric acid emits highly toxic and corrosive sulphur oxide gases. Dangerous corrosive gases are also formed when water is mixed with sulphuric acid. A jet of water is therefore not an appropriate method of extinguishing a fire where sulphuric acid is stored. Suitable extinguishing media are foam, dry powder, carbon dioxide and dry sand.

Transport of dangerous goods

The transport of dangerous goods by road, rail or inland waterway presents a considerable risk of accidents. Measures should therefore be taken to ensure that such transport is carried out under the best possible conditions of safety. These are regulated in EU-legalisations and in national laws.

Directive 2008/68/EC of the European parliament and of the council of 24 September 2008 on the inland transport of dangerous goods.

European Agreement concerning the International Carriage of Dangerous Goods by Road. ADR[15]is applicable from 1 January 2013. UNECE.

The carriage of dangerous goods is subject to international regulations for packaging and labelling, and for how the goods are to be transported. The ADR[25] regulations apply to the international and national carriage of dangerous goods on and off-road, and therefore apply throughout the EU.

How sulphur acid is classified as dangerous goods

Sulphuric acid is classified as dangerous goods under these **designations: UN number 1830 (>51% acid) and UN number 2796 (≤51% acid), packing group II** (visible necrosis after exposure for 3-60 minutes and within 14 days' observation), **hazard class 8 and transport class 2**. ADR regulations therefore apply. However, sulphuric acid is not classified as a chemical subject to the Seveso Directive[16].

Multiple parties may be involved in the transport of dangerous goods. It is therefore especially important to specify who is responsible for what, as described in ADR[25]. The main parties are considered to be the consignors, carriers and consignees. Others include packers, loaders, fillers and the operators of tank containers, UN portable tanks and tank wagons.

Alongside carriage, the transport of dangerous goods also includes loading and unloading including storage and the handling of dangerous goods in connection with transportation.

It is important to be aware that once sulphuric acid is mixed into slurry in the proportions of a few litres per cubic metre of manure, the mixture is not considered corrosive. According to ECHA[17], sulphuric acid is classified as corrosive only if the solution is 15% or stronger. A weaker solution, i.e. acidified slurry, is therefore not classified as corrosive provided there are no other substances in the solution that may affect its corrosivity.

ADR driver training certificate

Sulphuric acid is classified as dangerous goods, so ADR training is required to be permitted to transport it. Drivers that transport dangerous goods by road must have undergone valid driver training and hold a valid ADR certificate. The ADR certificate

[15] ADR is the abbreviation for the *European **A**greement Concerning the International Carriage of **D**angerous Goods by **R**oad.*

[16] Directive on measures to prevent and limit the consequences of serious chemical accidents (Seveso).

[17] https://echa.europa.eu/sv/information-on-chemicals/cl-inventory-database/-/discli/details/9111

confirms that the driver has completed driver training and has passed the training course successfully.

Exceptions from ADR

However, there are **exceptions** for special circumstances based on the value calculated quantity, limited quantity[18] or reduced quantity. Reduced quantity is not addressed here. Also, some countries have exceptions from required ADR-training that can be applied on transporting sulphuric acid in IBCs with tractors. Check national regulations for your country.

Exemptions related to quantities carried per transport unit

One way to transport dangerous goods with some relief from the regulations in ADR is to use the rules on *exceptions related to quantities carried per transport unit* **[19]**. The method can be used when the transfer takes place only within an area where dangerous goods are manufactured, stored or used.

Sulphuric acid is in transport Class 2. The total quantity of acid transported is therefore to be multiplied by a factor of 3 in accordance with the table. For sulphuric acid, the result value must be max. 1000, to allow transportation under this exemption. The calculations show that a maximum of 333 litres[20] of sulphuric acid may be transported under the exemptions of quantities carried per transport unit. The driver only needs 1.3 training. The load must be in a labelled type-approved container carrying the symbol

The goods declaration must accompany the load. The vehicle must be equipped with at least one fire extinguisher with a minimum capacity of 2 kg dry powder. The load must be secured, and regulations covering how it is loaded, unloaded and handled must be available.

The goods declaration must include information on the total and calculated quantities. For 96% sulphuric acid, this could be:

UN 1830 Sulphuric acid, 8, II, Corrosive Transport class 2: 333 litres (value 999).

Limited quantity

In this instance, the sulphuric acid must be packed in max. 1 litre containers and in cardboard boxes to max. 30 kg per package (including the weight of the packaging).

[18] https://www.msb.se/RibData/Filer/pdf/26565.pdf
[19] ADR, Annex A, chapter 1.1.3.6
[20] The value is below 1000, i.e. 333 litres multiplied by 3 = 999.

The total weight of all the packages must not exceed 8 tonnes. This requires 1.3 training. Since each movement is less than 8 tonnes, the vehicle need not carry dangerous goods symbols. However, the packages must be labelled with the symbol shown below, and with directional arrows because a liquid is being carried.

This exemption is unpractical to apply on acidification of slurry on a farm because of the limitation on max. 1 litre packages (Fig. 7).

Fig. 7. Example of goods for transportation with limited quantity of liquid. From MSB, Transport av farligt gods, Väg och järnväg 2015/2016.Publ.no: MSB805 – March 2015, ISBN: 978-91-7383-531-2 (in Swedish).

Education ’1.3 training’

The transportation of dangerous goods under certain exemptions and reliefs, exemptions related to quantities carried per transport unit limited and reduced quantities, does not require driver training with an ADR certificate. However, the requirements of what is known as 1.3 training must be met. In addition to transportation, the training requirement also applies to persons that (for example) pack, load or unload dangerous goods, and to others whose tasks relate to the transport of dangerous goods, in this instance by road.

The purpose of the training is to educate personnel about the risks and dangers associated with the dangerous goods, and the applicable regulations. A detailed description of all completed training, including refresher courses, must be retained by the employer for at least five years, and be made available upon request by the employee or the authority responsible. Training documentation must be verified when a new employment begins. For example, the documentation may consist of the employer having training records and the employee having a certificate. If a person is to perform tasks they are not trained for, this may only be done under the supervision of a trained person. The training has three parts (relating to sulphuric acid): **General Awareness Training** in the provisions for the carriage of dangerous goods; **Task-specific training** in the provisions commensurate with the duties and responsibilities of the personnel; and **Safety training** in the hazards and dangers that dangerous goods can present in the activities of the personnel during transportation, loading and unloading.

Training is repeated every two years to take account of changes to the regulations, which occur at the same frequency. The employer must retain a detailed description of the training for five years.

Safety adviser

The obligation to have a safety adviser applies to each undertaking the activities of which include the carriage or the related packing loading, filling or unloading, of dangerous goods by road.[21]. All those directly involved in the transport of dangerous goods must have an adviser, as must both consignors and carriers. Nevertheless, there are exemptions for the transportation of value calculated or limited quantities. However, having a safety adviser for discussing regulations and precautionary measures is recommended.

Accident statistics

The slurry acidification method is not yet applied in Europe with exception of Denmark, so there are no specific statistics on accidents or serious incidents. Neither does the Danish report on the status of slurry acidification mention anything about accidents that have occurred during the process (SEGES, 2015).

In general

Laws and regulations change over time. Always check with national and local authorities for up-to-date regulations.

[21]ADR, Appendix A, chapter 1.8.3

Country specific regulations and conditions

Author: Henning L. Foged

Denmark

The following guidelines for handling and storing of sulfuric acid is among other based on recommendations from Domino [22]and Lyngvig and Strudsholm[23].

General aspects

Concentrated sulfuric acid is an aggressive and dangerous chemical (fig. 8). By organising the place where sulfuric acid is handled and stored, and with the proper personal protective equipment and training, the risks for accident and their severity can be minimised.

Fig. 8. Pictogram for etching acid.

Personal safety

Sulfuric acid corrodes the skin severely and causes burning pain, redness, blisters and chemical burns.

If the eyes have been splashed with sulfuric acid, deep etching, tearing, eyelid cramps and consequent risk of serious eye damage with a loss of vision occur.

If you breathe sulfuric acid mist, it causes pain in the nose, mouth and throat. If the sulfuric acid mist is concentrated, it can lead to fatal pulmonary oedema (accumulation of fluid in the lungs).

If you by accident have drunken sulfuric acid, searing of mouth, oesophagus and stomach will happen. The result is pain, difficulty in swallowing, anxiety and bloody vomiting. In and around the mouth there are brown spots and aesthetic ulcer.

Protective measures are:

- Wear goggles or face shield.
- Use Camatril gloves approved according to EN374 and with a L underneath the flask.
- Use Tychem C-suit or Tychem C apron with sleeves and throats if the sulfuric acid is above 30 percent concentration.
- If the sulfuric acid is below 30 percent concentration, a Tychem Classic suit or apron is sufficient.
- Use Nitrile rubber boots.
- Wear full or half-mask with a type E2 gas filter.

[22]Domino, Helle Birk. 2016. Sådanhåndtererogopbevarer du svavelsyre. https://www.landbrugsinfo.dk/tvaerfaglige-emner/arbejdssikkerhed/sider/saadan_haandterer_og_opbevarer_du_svovlsyre.dotx.aspx

[23]Lyngvig, Henning Sjørslev and Karin Strudsholm. 2011. Gylleforsuring - sikkerhed og regler ved håndtering af svovlsyre. Videncentret for Landbrug.

- Be sure to have plenty of eye wash at hand.
- Check that the emergency shower is close - and works.
- Wash hands, forearms and face thoroughly before eating, smoking or going to the toilet.
- Change the tractor's front tank close to an emergency shower.
- Work with pallet tanks should only be done when two persons are present.

In case accident have happened:

- Remove contaminated clothing immediately. Rinse skin thoroughly with cold water
- Open the eye at maximum, remove any contact lenses and rinse with water (preferably from an eye rinse). Continue the rinse for at least 15 minutes or until a doctor takes over the treatment
- Provide fresh air if the accident has occurred indoors.
- Rinse mouth thoroughly if sulfuric acid has been swallowed.
- Drink plenty of water and do not induce vomiting.
- Call an ambulance or seek a doctor.

Storage

Sulfuric acid is an aggressive and dangerous chemical. Therefore, you should observe the following guidelines for handling and storing it:

Fig. 9. The UN number for sulfuric acid is UN 1830 (class 8, packing group II).

- Only buy sulfuric acid in pallet tanks that are UN approved (the density of sulphur is 1.84. You cannot be sure that companies using unauthorised pallet tanks takes this into account).
- Get pallet tanks with sulfuric acid delivered immediately before use, and order only the amount you expect to use for the task. Avoid storing concentrated sulfuric acid over longer periods, and keep stocks as low as possible.
- Keep pallet tanks in a place that is designed for the purpose. The place must be marked so that there is no danger of vehicles collision of it. Keep the pallet tanks under roof in a cool place with good ventilation. Sulfuric acid expands 10 percent if the temperature rises from -5 to 25 °C. Therefore, pallet tanks must not be completely full.
- Make sure the pallet tanks are tightly closed and that the safety valve is properly functioning, so that the pressure in the tank can be equalised continuously.
- The supplier of sulfuric acid has responsibility to inform about proper storage of the acid.

Storage of chemicals, including sulfuric acid, is covered by Annex 2, item D201 of the Order of Approval, and must therefore have an environmental approval.

However, temporary storage of up to 20 cubic meters of sulfuric acid must not necessarily be approved. But it is anyway required that the acid is kept environmentally safe, i.e. with the possibility of collecting spill from the largest container at a place without floor drainage.

Fig. 10. A double polyethylene collection box (PE), equipped with openings forklifts and lifts.

A temporary storage should not be placed in groundwater sensitive areas.

Spillage:

- It must be possible to collect spillage / leakage, e.g. by placing pallet tanks over a PE collection pool that can hold the entire content of the pallet tank if an accident happens.
- Establish an emergency shower and an eye rinsing station where the sulfuric acid is stored / handled. Check the emergency equipment regularly.
- You can stem up and collect spilled sulfuric acid with sand, cats gravel or other absorbent material. Then throw it into waste containers that are suitable for the purpose.
- Sulfuric acid must not be stored together with highly basic substances, chlorine products, oils, solvents or organic substances such as sawdust, wood and textiles.

If you by accident has punctured a pallet tank with the forks of a telescopic loader or tractor, consider - before pulling the forks out - whether it is best to tilt the pallet tank with the forks as they are sitting, or rather pull the forks out and place them differently to get the tilted pallet tank onto the side so that the holes would sit as high as possible.

If sulfuric acid is wasted, you can do the following:

- Sprinkle sand or soil over the wasted acid.
- If the spill is on a concrete floor, wooden floor or masonry, you can rinse with ample amounts of cold water. If there is no water available, the acid can be neutralized with lime, chalk, soda or salmiac spirits. But be careful: There is a risk of excessive reaction with concentrated sulfuric acid.
- Contact the supplier of the sulfuric acid so that they can empty the leaking pallet tank with special equipment.

Contact the local environmental authorities if the discharge has occurred close to a drinking water drilling.

Transport of dangerous goods

An ADR certificate is required, even if the transport is carried out by tractor between the farm and its fields. However, it is allowed to transport an amount below 333 litres with a registered vehicle without ADR certification. In any case, requirements for marking, carry of transport documents and safety equipment is required according to safety instructions and the driver must be chapter 1.3 trained. The training certificate

must be kept by the employer. Moving pallet tanks on the farm area is not covered by the ADR rules. All types of agricultural tractors used for transport of an acidification system between the farm and their own fields are not subject to the ADR rules and may therefore be carried out without an ADR certificate. Unregistered, unauthorized tractors on machine stations used for slurry acidification are not subject to the ADR rules and may therefore be operated without the ADR certificate. Registered tractors must also be used for driving with the acidification equipment. The reason for this is that manure transports does not require the tractor to be registered. Therefore, when the tractor and slurry tanker runs together, the tractor is considered not to be registered. In both cases, the same tractor must not be used for transporting sulfuric acid alone. A tractor with a front-mounted sulfuric acid tank is subject to ADR rules and must not drive on public roads without ADR certificates.

Examples – Scenarios for Denmark

In-house acidification: The farmer would not normally come into contact with the acid and therefore normally not have risks for coming into contact with the acid. The acid is store in double walled tanks, that are filled up by the special trained and ADR certified truckers that deliver the sulfuric acid on the farm. The storage tanks on the farm has in most cases pollocks to prevent vehicles to collide with them. The tanks are marked with pictograms for etching acid and has an emergency shower.

In-storage acidification: People that handles the acidification equipment must have full body protective gear, meaning wearing full-face mask, body suit, boots and gloves. The equipment must be equipped with have an emergency shower. The acid is delivered by special trained and ADR certified truckers.

In-field acidification – BioCover'sSyreN system: Safety goggles and gloves must be used during change of pallet tanks.

In-field-acidification – KyndestoftAcidLine system: The method of protection of persons during slurry acidification is the same as "In-storage" SAT described above.

Literature

- Domino, Helle Birk. 2016. Sådan håndterer og opbevarer du svovlsyre. https://www.landbrugsinfo.dk/tvaerfaglige-emner/arbejdssikkerhed/sider/saadan_haandterer_og_opbevarer_du_svovlsyre.dotx.aspx
- Lyngvig, Henning Sjørslev and Karin Strudsholm. 2011. Gylleforsuring - sikkerhed og regler ved håndtering af svovlsyre. Videncentret for Landbrug.

Estonia

Author: Kalvi Tamm

General aspects

The specific safety requirements from labour safety point of view in Estonia are regulated by Occupational Health and Safety Act (*Estonian*: *Töötervishoiu ja tööohutuse seadus*). The act has regulation about "The maximum limit of parameters of chemical hazards" (*Estonian*: *Töökeskkonna keemiliste ohutegurite piirnormid*).[24] Sulfuric acid safety aspects are described on safety data sheet. (Roth)[25,26]

Personal safety

By the safety data sheet the sulphur acid containers are labelled according to Regulation (EC) No 1272/2008 (CLP).

Hazard statements

H314 Causes severe skin burns and eye damage.

Precautionary statements - prevention

P280 Wear protective gloves/protective clothing/eye protection/face protection

Required is sufficient amount fresh water and tools to rinse body parts, what get contact with sulfuric acid.

Precautionary statements - response
P301+P330+P331 IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
P303+P361+P353 IF ON SKIN (or hair): take off immediately all contaminated clothing. Rinse skin with water/shower.
P305+P351+P338 IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P310 Immediately call a POISON CENTER/doctor.

[24]https://www.riigiteataja.ee/en/eli/505052017007/consolide
https://www.riigiteataja.ee/aktilisa/1301/1201/1011/VVm_293_lisa_uus.pdf#
[25]Textin Estonian: https://www.carlroth.com/downloads/sdb/et/4/SDB_4623_EE_ET.pdf
[26]Text in English: https://www.carlroth.com/downloads/sdb/en/4/SDB_4623_GB_EN.pdf

Description of first aid measures

General notes
Take off immediately all contaminated clothing. Self-protection of the first aider.

Following inhalation
Provide fresh air. In all cases of doubt, or when symptoms persist, seek medical advice.

Following skin contact
After contact with skin, wash immediately with plenty of water. Immediate medical treatment required because corrosive injuries that are not treated are hard to cure.

Following eye contact
In case of contact with eyes flush immediately with plenty of flowing water for 10 to 15 minutes holding eyelids apart and consult an ophthalmologist. Protect uninjured eye.

Following ingestion
Rinse mouth immediately and drink plenty of water. Call a physician immediately. If swallowed danger of perforation of the oesophagus and the stomach (strong corrosive effects).

Most important symptoms and effects, both acute and delayed
Corrosion, gastrointestinal complaints, cough, risk of blindness, gastric perforation, risk of serious damage to eyes, vomiting, dyspnoea.

Indication of any immediate medical attention and special treatment needed
Treat symptomatically.

Handling
Precautions for safe handling
When diluting/dissolving, always have the water ready first, then slowly stir in the product. Handle and open container with care.

Advice on general occupational hygiene
Wash hands before breaks and after work. Keep away from food, drink and animal feeding stuffs.

Short-term exposure limit for vapour 3 $mg \cdot m^{-3}$: a limit value above which exposure should not occur and which is related to a 15-minute period unless otherwise specified.

Time-weighted average (long-term exposure limit) for vapour 1 $mg \cdot m^{-3}$: measured or calculated in relation to a reference period of 8 hours' time-weighted average.

Time-weighted average (long-term exposure limit) for sulphur acid fog 0,05 $mg \cdot m^{-3}$. The fog is defined by the fraction of particles reaching to the upper respiratory tract.

Individual protection measures (personal protective equipment)
Eye/face protection

Use safety goggle with side protection. Wear face protection.

Hand protection
Wear suitable gloves. Chemical protection gloves are suitable, which are tested according to EN 374. Check leak-tightness/impermeability prior to use. For special purposes, it is recommended to check the resistance to chemicals of the protective gloves mentioned above together with the supplier of these gloves.

- Type of material and thickness: FKM: fluoro-elastomer, 0.7mm.
- Breakthrough times of the glove material*:* >480 minutes (permeation: level 6)
- Other protection measures: take recovery periods for skin regeneration
- Preventive skin protection (barrier creams/ointments) is recommended.

Respiratory protection
Respiratory protection necessary at: Aerosol or mist formation. P2 (filters at least 94 % of airborne particles, colour code: White). Observe the wear time limits according GefStoffV in combination with the rules for using respiratoryprotection apparatus (BGR 190).

Storage

Conditions for safe storage, including any incompatibilities
Keep container tightly closed.

Incompatible substances or mixtures
Observe hints for combined storage.

Ventilation requirements
Use local and general ventilation.

Specific designs for storage rooms or vessels
Recommended storage temperature: 15 - 25 °C.

If there is over 100 t of sulfuric acid in the farm in one time moment then the farm is classified as high-risk enterprise and should have safety advisor.

Transport of dangerous goods

The drivers driving tank trucks to transport sulphur acid have to participate ADR training.

There is no information about any other special training required for operators working with sulfuric acid.

The transport of sulphur acid is regulated by Road Transport Act. (*Estonian: Autoveoseadus*).

Rules for the carriage of dangerous goods (*Estonian: Ohtlike veoste autoveo eeskiri*) says that sulphur acid over 51% is dangerous good. The transporter has sign of danger 8.

Prohibited to drive in E-category tunnels.[27] Transportation information is also described on safety data sheet.

Examples – Scenarios for Estonia

In-house acidification

The farmer would not normally come into contact with the acid and therefore normally not have risks for coming into contact with the acid. The acid is store in double walled tanks, that are filled by the certified truckers that deliver the sulfuric acid on the farm. The storage tanks on the farm has in most cases bollards to prevent vehicles to collide with them. The tanks are marked with pictograms for etching acid and has an emergency shower.

In-storage acidification

Employees operating the acidification system must have full body protective (body suit, boots and gloves, transparent mask of face). The equipment must be equipped with have an emergency shower. Sulfuric acid is supplied by truck drivers with ADR certificate.

In-field acidification

Work safety rules and clothing the same as in case of the "in-storage" system discussed previously.

BioCover's SyreN system. Safety goggles and gloves must be used during change of pallet tanks.

Kyndestoft AcidLine system. Persons operating equipment to the slurry acidification must have and use protective clothing and full-face mask.

[27]https://www.riigiteataja.ee/en/eli/505022016005/consolide
https://www.riigiteataja.ee/akt/110062011019?leiaKehtiv

Finland

Author: Sari Peltonen

General aspects

Handling and storage of sulphuric acid are under the statutes of the council of state concerning handling dangerous chemicals and control of storage conditions (685/2015) and safety requirements of industrial handling and storage of dangerous chemicals (856/2012). Safe handling of sulphuric acid doesn't presume any special measures when the substance is handled as required.

No permission is required from Finnish safety and chemical agency (Tukes)[28] to obtain sulphuric acid. An announcement to rescue authorities can be done with a form that every rescue department has their own. Also, a form which can be found from Tukes website can be used. Sulphuric acid is classified as a corrosive chemical and that must be considered in the announcement. Sulphuric acid is a starting material of explosives, whose marketing and consumption is controlled by the European parliament's and council's statute (EU) No. 98/2013, but it is not that kind of starting material which would demand a permission from a police force when it is used in business activity or industrial and commercial activity.

In Finland, there have been done research where slurry has been acidified with sulphuric acid, and the amount of acid used is about 3-5 litres per 1000 kg slurry. This means that in big cattle farm the used amount of sulphuric acid per year would be 10 000 – 20 000 litres. In-field acidification of the slurry could be suitable for contractors to do. In that case, the annual amount of handled and stored sulphuric acid would be much bigger in volumes if the contractor did the work as so called turnkey way. The operation has no obstacles if the required announcements, possible licenses and qualifications of safe operation have been taken care of. Based on the operative criterion sulphuric acid is not classified as hazardous to the nature, but it has been found to be harmful for aquatic biota.

Personal safety

When handling sulphuric acid, a respirator equipped with P2-filter must be used. The material of used gauntlets must be strong and impervious to sulphuric acid. When choosing gauntlets the permeability time, permeability factor and deterioration must be taken into account. The permeability of the gauntlets must be checked from the manufacturer. The material and other qualitative properties affect the election of the gauntlets and these properties vary between different manufacturers. For the protection of eyes and skin it must be used protective goggles that are tightly settled in and suitable protective clothing. International agency for research on cancer (IARC) has classified fogs from inorganic acid that contain sulphuric acid carcinogenic (group 1).

[28] http://www.tukes.fi/en/Tieto-meista/

Storage

Sulphuric acid must be stored so that the containers are tightly closed. Sulphuric acid must be stored apart from reducing agents and inflammable matter. Finnish safety and chemical agency (Tukes) controls large-scale handling and storage of dangerous chemicals. The permission limit for corrosive chemicals like sulphuric acid is 1000 tonnes. As for rescue authorities, they control minor handling and storage of dangerous chemicals. The limit for minor chemical handling or in other words the operation that requires announcement to rescue authorities is 10 tonnes. For this figure, all chemicals in the farm must be considered, also e.g. formic acid, fuels and plant protectants, not only sulphuric acid.

When storing sulphuric acid, it must be taken care of that the acid is handled properly, and it won't be mixed with any other chemicals even if the container breaks down. With sulphuric acid, you must make sure that in case of for example overfilling, corrosion or any other damage the acid won't get to the environment.

Sulphuric acid is not needed to be stored in a locked room, unless violence is a potential threat. In that case, the rescue authority may require locks or access control system. Sulphuric acid must be stored away from food and feed stuff.

The materials of warehouse where the sulphuric acid is stored must be considered, because sulphuric acid reacts with strong bases and strong sulphuric acid reacts fast with several metals. Strong sulphuric acid releases toxic gases from cyanides, sulphides and carbides. The reaction between sulphuric acid and chlorates, perchlorates and potassium permanganate can cause an explosion because of released oxygen compounds. Sulphuric acid corrodes quickly aluminium, copper and compounds that includes those metals. In reactions with metals there can be generated inflammable hydrogen gases. Organic matter, especially those that include hydrogen and oxygen, for example paper and cotton can become charred and may easily catch fire. The concrete destruction process increases with a decrease in H_2SO_4 concentration below 93%.

In case of accidents the sulphuric acid that has for example flown down to the ground does not evaporate at all because of the humidity of the soil which promotes the absorption of the acid into the ground. Small amounts of sulphuric acid can be soaked in commercial absorption materials and collected to covered containers to be neutralized. Waste of sulphuric acid can be neutralized with lime. Impounded sulphuric acid must be collected and acid that stays on the ground must be neutralized and the surface of the ground must be skimmed off.

Transport of dangerous goods

In road transport, sulphuric acid is classified as corrosive substance (class 8). The purpose of transport legislation of dangerous goods is to prevent and hinder damage and danger that transportation may cause to people, environment and property. The containers and packages of dangerous goods must meet all chemical-related technical demands so that the content doesn't cause any danger to people or environment even

in case of accident. Tukes controls that the containers and packages that are used in transportation fulfil the demands.[29]

The vehicle that is used to transport dangerous goods must be suitable specially to transport dangerous goods by its structure, technical qualities and equipment. Furthermore, the road tanker that is used to transport dangerous goods and the vehicle that is used to transport explosives must get approved (VAK[30]-approval) and after that it must be inspected every year (VAK-inspection), if more than minor amounts of sulphuric acid is transported with it. The driver must make sure that the vehicle is properly manned and loaded. It is also important to make sure that transportation is performed under the regulations and orders that are valid for transportation.

In case of duty that is related to transportation and temporary storage of dangerous goods, the employee must make sure that the employer has proper education or qualification for the job. The employee must have all the knowledge about the education or qualification and the information about them must be presented to the supervising authority if asked to make sure that the education is enough considering the duty of the employer. If the transported material, amount of it or vehicle demand special know-how, the driver must have a special license to transporting dangerous goods as well as the regular driver's license. In the vehicle, all crucial information from the transported goods must be presented to ensure the safety in case of accident or danger.

In the basis of a municipality's reasonable proposal, Finnish Transport Safety Agency (Trafi) can limit transportation of dangerous goods in certain areas, roads or parts of the road, if the transportation can cause remarkable danger for people, environment or property. When imposing the limitation, it must be taken care of that transportation of dangerous goods is not limited more than needed to prevent a danger. The municipality must inform about the limitation concerning its area.

Summary

- Safe handling of sulphuric acid doesn't presume any special measures when the substance is handled as required.
- The operation has no obstacles if the required announcements, possible licenses and qualifications of safe operation have been taken care of.
- International agency for research on cancer (IARC) has classified fogs of inorganic acid that contain sulphuric acid as carcinogenic (group 1).
- Finnish safety and chemical agency (Tukes) controls large-scale handling and storage of dangerous chemicals.
- The permission from Tukes is not obligatory to obtain sulphuric acid.
- The permission limit for corrosive chemicals such as sulphuric acid is 1000 tonnes.
- The limit for minor chemical handling or in other words the operation that requires announcement to rescue authority is 10 tonnes.

[29] http://www.tukes.fi/en/Branches/Chemicals-and-gas/Transport-of-dangerous-goods/
[30] VAK – Finnish: Vaarallisten aineiden kuljetus (English: Transport of dangerous goods)

- When storing sulphuric acid, it must be taken care of that the acid is handled properly, and it won't be mixed with any other chemicals even if the container breaks down.
- Sulphuric acid is not needed to be stored in a locked room.
- In case of accidents the sulphuric acid that has for example flown down to the ground does not evaporate at all because of the humidity of the soil which promotes the absorption of the acid into the ground.
- In road transport, sulphuric acid is classified as corrosive substance (class 8).
- The containers and packages of dangerous goods must meet all chemical-related technical demands so that the content doesn't cause any danger to people or environment even in case of accident.
- Tukes controls that the containers and packages that are used in transportation fulfil the demands.
- Furthermore, the road tanker that is used to transport dangerous goods and the vehicle that is used to transport explosives must get approved (ADR/VAK-approval).
- In case of duty that is related to transportation and temporary storage of dangerous goods, the employee must make sure that the employer has proper education or qualification for the job.
- In the basis of a municipality's reasonable proposal, Finnish Transport Safety Agency (Trafi) can limit transportation of dangerous goods in certain areas, roads or parts of the road, if the transportation can cause remarkable danger for people, environment or property.

Examples – Scenarios for Finland

In Finland in-storage and in-field acidification SAT techniques are the most probable ones. In these cases, full body protective gear must be worn. That means full-face mask, body suit, boots and gloves. The emergency shower must be available. The acid is delivered by special trained and ADR/VAK-approved certified transport vehicles.

In in-house acidification SAT technique, the farmer usually comes not into contact with the acid but the acid transported to the farm and the tanks are filled by special trained and ADR/VAK-approved certified transport vehicles. The emergency shower must, however, be available.

Germany

Author: Sebastian Neumann

General aspects

Sulfuric acid must be handled in strict compliance with existing regulations regarding transported quantities, intended usage or form of transport. In Germany, different safety regulations apply for hazardous material (hazmat) which are classified into different categories (hazard classification).

Transport of sulfuric acid is not classified as hazardous material transport (hazmat transport) if following regulations are observed:

- Maximum design speed of vehicle must not exceed 25 km/h.
- Transported amount must not exceed 5 kg/5l or 30 ml/1000 ml
- No transport in public areas.

The European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) contains a special regulation that applies to craftsmen (and private persons) according to which craftsmen are allowed to carry small amounts of sulfuric acids for work purposes (e.g. measurement, repair and maintenance) on condition that safety precautions are considered, e.g. appropriate securing of cargo, surface of container must be free of adhering residues, no transport of damaged containers, driver instruction. This special regulation does not apply in case of internal or external provisioning of sulfuric acid. In this case transports are classified as hazmat transports. In additional, quantities mentioned in ADR section 1.1.3.1 must not be exceeded.

In the case of acidification of slurry and its application to farmland, transports not classified as hazmat transports may only carry the relatively small amount of sulfuric acid of maximum 333 l. In practice, acidification of slurry proved to be uneconomic considering the limitation to 333 l sulfuric acid and the maximum transport speed of 25km/h. An economic application of slurry acidification technology (SAT) is only conceivable if transport and application is compliant with ADR regulations. Consequently, only large farms or agricultural contractors are in the position to implement this technology since effort and expenses for certification according to ADR standard would be too huge to handle for regular farms. However, this aspect does not have to be disadvantageous since state-of-the-art technology is employed, which is not available to regular farms. Against this background, it is important to know that in Germany sulfuric acid is added during field application only, since acidification in barns or storages is currently not permitted by other regulations (see storage).

Personal safety

As shown, in Germany acidification of slurry is legally permissible during field application only. In order to guarantee personnel safety, storage (on the part of farmer or contractor) and transport have to comply with ADR regulations. In addition, vehicles must be provided with protective equipment (fire extinguisher, protective clothing, etc.) and drivers must be trained at regular intervals/have to regularly attend

training courses to obtain /renew their hazmat transport driver permit. The storage of sulfuric acid in IBC tanks does not require any further precautionary measures.

Storage

Relevant for this project is how farmers and contractors can provide safest storage. As a relatively simple solution, sulfuric acid can be directly stored in IBC tanks, since it is allowed to store up to 11 tanks without additional requirements. Special precautions are not necessary (e.g. environmentally sealed storage locations, emergency showers). For all practical purposes only a timely replacement of empty tanks must be ensured. More important for this project is the question of how to store acidified slurry properly and safely. In Germany, storage of slurry, liquid manure, silage effluent, and fermentation residues is laid down in the Ordinance on Installations for the Handling of Substances Hazardous to Water (*German: Verordnungüber Anlagen zum Umgang mit wasser gefähr denden Stoffen; AwSV*) from 18 April 2017. According to it, slurry, liquid manure, silage effluent, and fermentation residues may only be stored in leakproof and suitable plants (so-called JGS plants), on condition that no additives have been admixed. As a consequence, acidification of slurry in barns or manure tanks are not permitted at present. The fundamental concern behind this regulation is that the concrete walls of JGS plants could suffer from corrosion caused by sulfuric acid, which would lead to leakages. For this reason, field acidification is the only permissible technique, alternative methods are currently not permitted under German law.

Transport of dangerous goods

In the section General Aspects, it has been explained that transport of even small quantities of sulfuric acid, which are not yet subject to the dangerous goods legislation, must comply with certain rules. Transport of a maximum of 333 l of sulfuric acid by a transportation unit exceeding 25 km/h, must comply with the following regulations:

- Shipping papers (exception 18 GGAV);
- Packaging must be compliant with UN standards, hazard warning labels;
- Appropriate load securing;
- Fire extinguisher; 5 kg (sealed, date of next inspection);
- Smoking ban;
- Driver instruction through loading agent;
- Ventilation;
- Prohibition of opening packages;
- No transportation of damaged packages/containers;
- No access with open flame (smoking ban);
- Instruction of involved persons;
- Cleaning of soiled vehicles.

These regulations are relatively easy to follow, especially if IBC-tanks are used. At present two problems remain unsolved. On the one hand the quantity of 333 l is too

low to allow an economical operation (this is true for animal manures but especially for fermentation residues from biogas plants, since these have a considerably higher pH than manures and significantly more acid is required for lowering the pH). On the other hand, there is no transportation system for slurry acidification in Germany available permitting the combined transportation of sulfuric acid and slurry. The device currently borrowed from Denmark for the aim of this project is only for experimental purposes and currently not allowed for commercial use. This is not due to hazmat transport regulations, the ADR has set up uniform standards throughout the EU, but a direct result of the German Road Traffic Regulations (StVO). Due to the front attachment of the acid tank, the spacing between steering wheel centre and the front edge of the front tank exceeds 3.50 m (see figure 11).

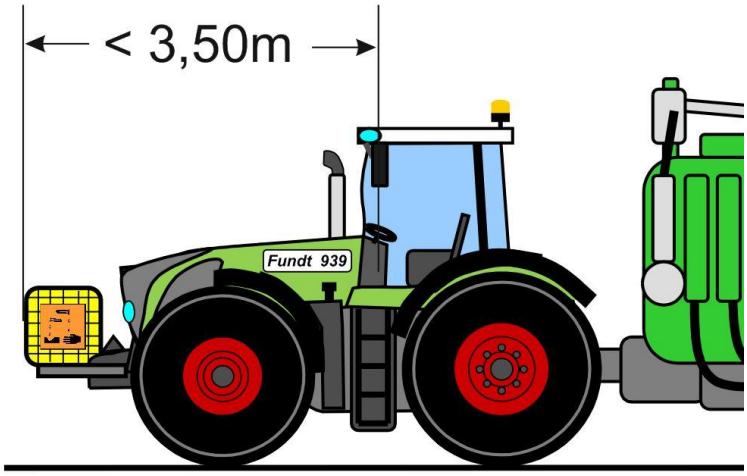


Fig. 11. German Road Traffic Regulations (StVO), a spacing between steering wheel centre and the front edge of the front tank which exceeds 3.50 m is not permitted

This is not permitted under the German Road Traffic Regulations and requires an exceptional permission. Exemption from this requirement may be granted (but must not necessarily), if in front cameras are installed, which allow the driver to see what is on the left and right of the vehicle via screens in the driver's cab. According to the law, these cameras can replace the assisting person who, at exits, driveways, field entrances etc. signal the driver a free road. Such cameras are compulsory for an exceptional permission but do not automatically guarantee that permission will be granted. Particularly in the case of sulfuric acid transport, it must be assumed that such exceptional permissions are not helpful to promote the implementation of animal slurry application and acidification technology (SATs). It must also be taken into consideration that in many regions of Germany hedge row sat field entrances impair visibility. This holds especially true for large parts of the federal state of Schleswig-Holstein.

For the transport of sulfuric acid destined for acidification, following two problems still remain unsolved.

1. The transportation limit of sulfuric acid must exceed 333 l.

The solution for the first problem is relatively simple. Transport must comply with the regulations stated in the dangerous goods legislation; ADRis applied in its entirety (see figure 12).

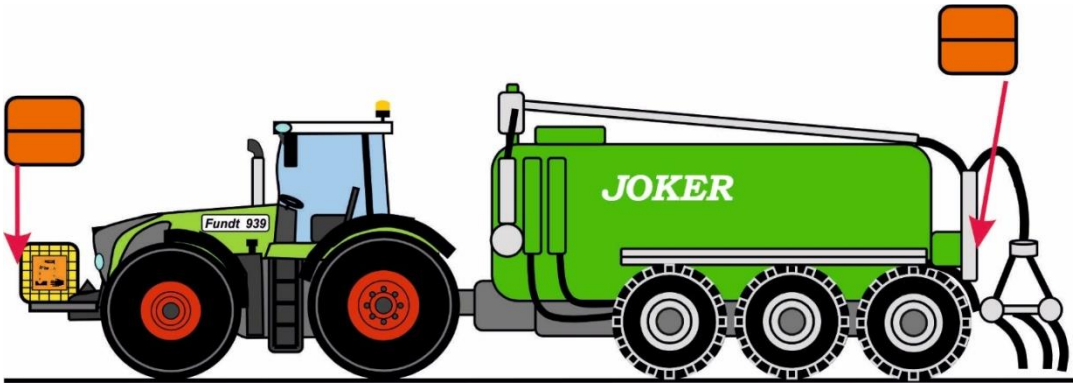


Fig. 12. Transport must comply with the regulations stated in the dangerous goods legislation; ADR is applied in its entirety, warning signs must be attached to the front and the rear of the transport unit.

Vehicles and drivers must meet the following conditions:

- warning signs attached to the front and the rear of transport unit,
- labelling,
- ADR-certification for trained drivers,
- ADR-equipment,
- Certified Package Cargo Papers,
- Instruction documents.

The fulfilling of these conditions is related to the cost of a few thousand euros. Large farms and contractors, however, will be in the position to meet these requirements.

2. The transportation unit used for acidification and application of slurry must comply with the German Traffic Regulations (StVO).

At present, it is difficult to meet this regulation, since there is no such vehicle or system on the market. Within the frame of this project and in cooperation with the manufacturer of slurry tanks, the intention is to design a slurry tanker for the transport of two IBC-tanks, mounted on the tanker, and which is equipped with the necessary acidification technology (SAT). SAT originates in Denmark and meets all legal standards of the UN and ADR.

The non-drip design of the tanks ensures an easy replacement of tanks and eliminates any risks for personnel and environment. The same conditions apply for the transport of IBC-tanks from manufacturer to agricultural contractor.

Summary of facts applying to Germany

The economic use of sulfuric acid for acidification requires strict compliance with ADR regulations for the transport of classified dangerous goods on the part of

suppliers and on the part of farmers or contractors. The vehicle used for acidification and application of slurry has to comply with the German Traffic Regulations (StVO). Since such slurry application machinery is currently not commercially available in Germany, it is the aim of this project to design and construct such a SAT prototype SAT tanker.

Examples – Scenarios for Germany

Currently, as stated above, acidification of slurry during land application is the only viable technique in Germany. In order to be able to meet the StVO requirements it is necessary to design and construct for the purpose of this project a slurry tanker, equipped with two additional tanks, applicable for the Danish SAT and filled with sulphuric acid, which are installed on the drawbar at the front of the tanker under carriage. For this purpose, to develop carrier frame designed to carry these two IBC tanks, has to be mounted on the drawbar at the front of the slurry tank under carriage. Two tanks are necessary, because acidification of fermentation residues from biogas plants is of special importance in Germany. This is due to the fact that pH of biogas residues is higher than pH of cattle or pig slurry and thus requires additional acidification. Towing vehicle, slurry tanker and driver must meet the regulations for the transport of hazardous materials (hazmat transportation regulations). The call for proposals has just been released. The technology of acidification to be mounted on slurry tankers has to be bought from Denmark (distributor, dosing device). At present, extensive scientific field trials are carried out to test the effect of acidified slurry. In addition, in-field acidification tests are carried out on field-scale by means of a front mounted implement, borrowed from Denmark (exception permit, not more than 333 l acid). It is expected that, by means of the first prototype of slurry tank, the technology will be available for commercial use in spring of next year, which would mark the beginning of in-field acidification in Schleswig-Holstein. Since quite a number of agricultural partners have expressed their interest in SAT, it is conceivable that with a functioning system further devices will be built. The acceptability will depend on one hand on the additional costs compared to present application techniques and on the other hand on the additional value for farmers as well as on the results of scientific tests.

Latvia

Author: Jānis Kažotnieks

General aspects

There were two options to go for diluted (50%) or concentrated (96%) sulphuric acid (Acid) to implement the project activities in Latvia. It was decided to use concentrated version, which all goes under Regulation (EC) 1272/2008 and the specific Latvian legislation act – Chemical Substances Law (29 October 2009).[31] The main objective of the law is to reduce the risk of harmful impact of chemicals to environment, humans and property. Acid there is defined as a dangerous substance – toxic or very toxic - to be treated and handled with proper care, which is then limited by law mentioned above.

There are some more legislation acts which regulates the Acid handling and requirements for the labour involved:

- Labour Protection Law (20 June 2001)[32],
- Cabinet Regulation No.1082 (30 November 2010) Procedure by Which Polluting Activities of Category A, B and C Shall Be Declared and Permits for the Performance of Category A and B Polluting Activities Shall Be Issued[33],
- Cabinet Regulation No.325 (15 May 2007) Labour Protection Requirements when Coming in Contact with Chemical Substances at Workplaces[34].

Personal safety

Personal safety when handling Acid is regulated by two legal acts in Latvia: Labour Protection Law (20 June 2001), and Cabinet Regulation No.325 (15 May 2007) Labour Protection Requirements when Coming in Contact with Chemical Substances at Workplaces. The main objective of these acts is to protect the employees from the risks of working environment.

There are some general requirements for the persons to handle acid:

- It is not allowed to handle Acid for the persons younger than 18 years.
- All the responsibilities to comply the requirements of safe work with Acid are under employer.
- Safety trainings have to be organised at work place at the beginning of employment and after each following year.
- Signature of employee in registration journal is required to prove the fact of training and following responsibilities during the work.
- Employees have to go through special medical examination annually to control their health parameters.

[31] https://likumi.lv/doc.php?id=47839
[32] https://likumi.lv/doc.php?id=26020
[33] https://likumi.lv/doc.php?id=222147
[34] https://likumi.lv/doc.php?id=157382

- It is obligatory for the employee to be informed about Acid properties (labels on the containers), the risk of explosion, effect on humans and environment as well as the danger of mixing in different substances, e.g., water or manure.
- Employees have to follow safe work and personal hygiene requirements to protect themselves and the surrounding environment.
- Handling Acid employees have to wear personal protection gear:
  - acid resistant rubber boots;
  - acid resistant zipped, safety sealed and hooded overalls;
  - acid resistant gloves;
  - acid resistant face masks with protection (gas) against Acid evaporations;
  - is strictly forbidden to eat, drink and smoke when handling Acid;
  - it is obligatory to have clean water tank within the manure spreader with acidification equipment on it;
  - it is recommended (not obligatory) to install emergency shower at the place of filling Acid;
  - it is not obligatory for employees to be able to give the first aid.

Storage

If more than 10 tonnes of acid are stored at the same time, then the storage of Acid is limited by Cabinet Regulation No.1082 (30 November 2010) Procedure by Which Polluting Activities of Category A, B and C Shall Be Declared and Permits for the Performance of Category A and B Polluting Activities Shall Be Issued[35]. Otherwise there are no limitations, except if Acid is stored in specially designed stationary storages, which is not really actual for Latvian situation.

Transport of dangerous goods

Tractor driver licence is needed for the tractor driver. And this is the only regulation, which has to be fulfilled transporting 1800 kg of sulphuric acid on public roads from farm to field as it is not defined as transport if acid is moved from farm to field. So, there are no regulations specified for transport on farm level, even if you transport 1.8 tons of sulphuric acid. This is in spite we are not allowed to transport even more than 100 litres of gasoline in a car having no special permissions for that.

Examples – Scenarios for Latvia

Company LaukuAgro will use in-field acidification technology, which is already purchased and tested in operation as a second hand SyreN system plus Sampson tanker with 24 m boom of trailing hoses. The acid will be transported from the dealer company in IBC's or in specially equipped container and then filled into IBC's on site. LaukuAgro will temporary (before and during spreading) store acid in IBC tanks and there are no special requirements for the storage of that. In spite of that they will equip the storage place with safe fencing. There'll be no storage during winter time and even summer

[35] https://likumi.lv/doc.php?id=222147

Lithuania

Author: Artūras Šiukščius

General aspects

In Lithuania, so far slurry acidification systems have not been used and there has been no wide usage of sulphuric acid in agriculture. These chemical elements have mostly been used in manufacturing fertilizers and, therefore, specialists and workers of agriculture are not familiar with the safety measures while working with sulphuric acid. In Lithuania, there are two the most perspective ways to use slurry acidification technologies: In-field and In-storage. Under In-field acidification technology, a farmer who has acquired a mobile slurry acidification system, injects concentrated (98%) sulphuric acid into the slurry during spreading. Slurry disposal in the fields requires to carry a container of concentrated sulphuric acid in front of the tractor, what is comparatively risky. It is also required to install a room or a yard for the storage of concentrated sulphuric acid.

In our opinion, various service companies could carry out slurry acidification in-storage containers. After acquisition of acidifying equipment, these companies could come to farms, bring concentrated sulphuric acid and complete slurry acidification in-storage. In this case, the service company would be responsible for the safety at working with sulphuric acid. Such companies could prepare workers and specialists to work with sulphuric acid much more effectively.

If slurry acidification technologies were applied in barns, special acidification systems by the barns and concentrated sulphuric acid tanks had to be additionally fitted, and safety would be responsibility of a farmer or animal keeper.

Carrying out the project ‘Baltic Slurry Acidification’ in Lithuania, we are planning to use concentrated sulfuric acid (98%) which has to be handled according to dangerous chemical materials safety data sheet. Sulphur acid is classified according to regulations (EB) Nr. 1272/2008 GHS05 corrosion Met. Corr.1 H290, which shows that sulphur acid can erode metals. The classification Skin Corr. 1A H314 shows that it can strongly burns skin and damages the eyes. Sulphur acid is also classified by council directive 67/548/EEB or directive 1999/45/EB C. Product (sulfuric acid (98%) is classifying and marking by directive (EB) Nr. 1272/2008.

Personal safety

Working with concentrated Sulphuric acid (98%) is considered to be dangerous and, therefore, only persons over 18 years of age having doctor’s permission (medical certificate) are allowed to work with it. Moreover, prior to working, a person has to be acquainted with the safety requirements regarding work with Sulphuric acid and his knowledge should be appraised by the Commission set up by head of institution. A certified labour safety specialist should be a member of the Commission. Following the person’s knowledge appraisal, he has to sign in the labour safety journal.

The worker has to know the physical and chemical qualities of concentrated Sulphuric acid, dangers in case of fire or explosion, the effect on human body and the

environment, changes when affected by water and air and how to act safely. The worker has to strictly execute safety and personal hygiene requirements, fire-prevention requirements and be disciplined. Besides, the worker has to be necessarily supplied with personal safety measures such as acid resistant gloves, footwear, protective goggles, overall and apron and special gas masks for protection of the breathing organs. Gas masks are individual by face, measurements and should be stored in a fixed and accessible place.

Personal safety measures should be neat and used for their proper purpose, protective clothes, clean. It is forbidden to wear dirty clothes, soiled with harmful, toxic, inflammable, etc. materials. At working place, it is forbidden to eat, drink and smoke. There should be an emergency shower fitted to wash oneself in case of body contact with dangerous chemicals. The worker should know hygiene requirements and be able to give first aid.

Storage

The storage of dangerous chemicals (Sulphuric acid 98%) is regulated by General requirements for storage of dangerous chemicals approved by Minister of Environment Protection of the Republic of Lithuania No 272 on December 22, 1998 and EC Directives and regulations.

According to the above regulations, these are the main requirements for Sulphuric acid storage:

- The territory should be fenced and protected day and night or have an alarm system. When the territory is fenced, a separate enclosure of the storehouse for chemicals is not required. At non-working hours, all the doors, windows and gates of the storehouse should be locked;
- Measures should be taken to collect rainwater, melting snow water from the territory surface that might be contaminated with chemicals during the working hours of the storehouse and in case of emergency situations. The collected water should be checked before getting into sewage, so it will not contaminate soil, surface and ground waters;
- All the access roads to the buildings, fire-escapes, anti-fire stock, firelocks and water pools should be unoccupied and orderly;
- In the territory, there should be signs indicating the direction of movement and engine parking sites.
- The entrance to the territory and the storehouse is forbidden for strangers and this should be indicated with a written warning;
- Anti-fire instructions for the materials and evacuation scheme should be hung on the wall of the storehouse. On the outer side of the storehouse door, signs should be hung describing how dangerous the materials stored are with respect to fire;
- Measures should be foreseen to prevent chemicals and contaminated water from getting uncontrolled into sewerage, contaminating the soil and surface or ground waters;
- The finish materials for the walls and ceiling of the storehouse should protect the building construction from the effect of chemicals, do not absorb dust and vapour. The ceiling and the walls should be cleaned easily;

- The protection of the facilities from lightning and static electricity charge should correspond to the standard requirements;
- Airing systems should be fitted according to the standard requirements. Their schedule and maintenance is regulated by separate instructions which indicate cleaning frequency of fire prevention measures, air passages, filters, valves and other devices, also actions of the staff in case of fire or emergency;
- Precautions should be taken at loading and unloading containers: do not break the tare with sharp objects, avoid falling, hitting, spilling of chemicals. It is forbidden to drag, toss and tumble the tare;
- Containers with concentrated Sulphuric acid should be stored in closed storehouses built from incombustible material or in separate isolated sections of the storehouse;
- The floor should be fireproof and corrosion resistant;
- Concentrated Sulphuric acid (98%) might be stored in collective yards, but the distance between the area with acid and other materials should be no less than 5 meters. Open yards should be protected from rainfall and direct sunlight;
- All the metal constructions of the storehouse should be painted with corrosion resistant paint.

Transport of dangerous goods

The concept "transport" by ADR and national law includes preparation of the dangerous consignment (identification, classification, packaging, and documentation), all loading operations, transportation and temporary storage. Therefore, all the transport partners (shipper, loader, driver, recipient, etc.) should be familiar with ADR requirements.

The driver carrying dangerous load must be a person not younger than 21 years of age and having B category driving license. The person must have attended courses at an appropriate educational institution, passed an exam and received a respective certificate issued by National Road Transport inspection by the Ministry of Transport and communications. Training and examinations are regulated by the order of the Minister of Transport and communications No. 3-336 of July 1, 2002.

All the partners of dangerous load transport are responsible for the proper conveyance. The transporter is responsible for the right qualification of the driver to carry dangerous goods by ADR certification, suitability of the vehicle and the necessary equipment to carry dangerous goods, provide information about the forbidden or recommended itinerary. The driver must check if the shipper presented all the documents: load documents, shipper's declaration, written instruction(s) in case of international shipment. The driver is responsible for stamping of the vehicle, safety of vehicle equipment and load fastening in the vehicle.

Examples – Scenarios for Lithuania

In Lithuania, three slurry acidification scenarios are possible and these are in-field, in-house and in-storage. If the system is used in-field, a farmer has to acquire the equipment and mounting it on a tractor and thereafter mix acid with slurry at its disposal in the field. This method is suitable when farmers keep slurry either in lagoons or in above ground circular tanks. Acid mixing with slurry in the field requires to carry one cubic meter-capacity container of concentrated sulphuric acid in front of the tractor

what increases safety requirements. However, in our opinion, this method is applicable.

If the system is used in-house, then should be special installation for concentrated sulphuric acid mixing and a container of concentrated sulphuric acid. This method is more suitable when building new farms and designing acidification systems on a farm.

If slurry is acidified in-storage, a farmer also has to acquire acidification system, but in this case, it would be more efficient if a qualified service were provided, including the supply of the acid for the farmer. This could reduce the risk of accidents because workers and specialists could be better instructed by the service company. Moreover, a farmer would not have to store concentrated sulphuric acid in his own territory.

Lithuanian University of Health Sciences is planning to use slurry acidification technology in- field, when slurry is acidified during the spreading with a slurry spreader tanker with a capacity of 20-25 m^3. It is intended to buy Biocover A/S system. This system requires a yard for storage of the containers with one cubic meter concentrated acid. In the course of a year, it is planned to buy up to 10 containers from a supplier according to the requirements. During the slurry spreading, the container with Sulphur acid will be attached to the tractor's front and carried to the fields together with slurry. The distance from slurry loading to its spreading will be 3-8 km. The tractor driver will be instructed by ADR requirements and will have a special certificate. Besides, the tractor driver and specialists working with Sulphur acid will be instructed regarding safety requirements by a labour safety specialist and their knowledge prior to work will be assessed by a university commission. The worker will have to confirm his instruction about labour safety in the journal for labour safety measures.

Poland

Authors: Witold Wardal, Marcin Majchrzak

In Poland, there are a number of legal EU regulations governing the treatment of chemicals, and in particular with concentrated sulfuric acid. First of all, there are the EU Regulation No 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC[36]. and Commission Directives 91/155/EEC[37], 93/67/EEC[38], 93/105/EC[39] and 2000/21/EC[40].

Polish legislation in relating to the safety at work with H_2SO_4 is harmonized with REACH and can be divided into the following groups: classification and general provisions, labelling, individual protection, measurements of harmful agents, waste management and packaging.

Classification, general regulations

- EU Regulation (EC) No. 1907/2006 (REACH)[41].
- Commission Regulation (EU) No 453/2010[42] of 20 May 2010 amending Regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH).
- Polish Act of 25 February 2011 on chemical substances and mixtures thereof (Journal of Laws of 2011, No. 63, item 322, as amended, and Journal of Laws of 2015, item 1953)[43].

Labelling

- Regulation of the Ministry of Health of 20 April 2012 on the labelling of packaging of dangerous substances and mixtures and certain mixtures (Polish Journal of Laws of 2004, item 445)[44].

[36] http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX:31976L0769
[37] http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex%3A31991L0155
[38] http://eur-lex.europa.eu/eli/dir/1993/67/oj
[39] http://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:31993L0105
[40] http://eur-lex.europa.eu/eli/dir/2000/21/oj
[41] http://eur-lex.europa.eu/legal-content/PL/TXT/?uri=CELEX%3A02006R1907-20140410
[42] https://www.theta-doradztwo.pl/images/akty_prawne/preparaty_i_substancje_chemiczne/ROZP_KOMISJI_UE_NR_453_2010.pdf
[43] http://dziennikustaw.gov.pl/du/2015/1953
[44] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20120000445

Individual protection

- Regulation of the Polish Ministry of Economy, Labour and Social Policy of 31 March 2003 on the essential requirements for personal protective equipment (Journal of Laws of 03.80.725)[45], as amended.
- Regulation of the Polish Ministry of Economy, Labour and Social Policy of 21 December 2005 on essential requirements for personal protective equipment (Journal of Laws of 05.259.2173)[46].

Measuring of harmful health factors

- Regulation of the Polish Ministry of Health of 30 December 2004 on occupational safety and health related to the presence of chemical agents in the workplace (Journal of Laws of 05.11.86)[47], as amended.
- Regulation of the Polish Ministry of Health of 2 February 2011 on the examination and measurement of occupational health hazards (Journal of Laws of 2011 item 166)[48].
- Regulation of the Polish Ministry of Labour and Social Policy of 6 June 2014 on the maximum permissible concentrations and intensities of agents harmful to health in the workplace (Journal of Laws of 2014, item 817)[49] as amended.

Waste management

- Polish Act of 14 December 2012 on waste (Journal of Laws of 2013 item 21)[50].
- Polish Act of 13 June 2013 on packaging and packaging waste management (Journal of Laws 2013, item 888)[51].
- Regulation of the Polish Ministry of the Environment of 9 December 2014 on the waste catalogue (Journal of Laws of 2014, item 1923)[52].

General aspects

EC Regulation 1907/2006 of the European Parliament and of the Council on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) requires the establishment of central technical, scientific and administrative control authority for various types of chemicals and chemical substances. In Poland, such role

[45] http://www.lex.pl/du-akt/-/akt/dz-u-2003-80-725
[46] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20052592173
[47] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20050110086
[48] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20110330166
[49] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20140000817
[50] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20130000021
[51] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20130000888
[52] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20140001923

is held by the Office for Chemical Substances, which is the central office supporting the Inspector for Chemical Substances[53].

According to Polish Art. No. 12 of the Act on Chemical Substances and their Mixtures (Journal of Laws of 2015, item 1953)[54], the tasks of the Inspector include in particular:

- collection of data on hazardous mixtures or mixtures presenting hazards and information provided by the European Chemicals Agency concerning substances;
- providing information on hazardous substances and mixtures of hazardous substances or substances presenting a hazard and mixtures presenting a threat to the medical and rescue services;
- perform the functions of the competent authority designated to perform the administrative tasks related to the export and import of hazardous chemicals as defined in the European Union regulations and to cooperate with other Member States of the European Union and the European Commission in this respect;
- dissemination of knowledge about the harmful effects of chemicals and their mixtures on human health and the environment, and knowledge about prevention of such impacts.

The National Information Center for Chemicals in Poland[55] has the following tasks and objectives:

- reply to industry inquiries – reference to specific articles of REACH regulation;
- help industry to understand their obligations under REACH & CLP;
- cooperation with other REACH & CLP consultation points;
- providing information useful for industry;
- providing expert advice on the responsibilities and obligations of manufacturers, importers and users under REACH.

Personal safety

Individual protection in the area of working with hazardous chemicals was determined in the Regulation of the Polish Ministry of Economy, Labour and Social Policy of 21 December 2005 on the essential requirements for personal protective equipment – PPE (Journal of Laws of 2005 No. 259 item 2173)[56].

PPE should:

- to provide sufficient protection against any threat;
- be designed and manufactured to ergonomics in such a way that under intended conditions of use for which they are planned, the user may normally perform all operations in the event of a hazard while using appropriate protection at the highest possible level. By protecting them at the highest possible level, which

[53] www.chemikalia.gov.pl
[54] http://dziennikustaw.gov.pl/du/2015/1953
[55] www.reach.gov.pl
[56] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20052592173

should be taken into account in the design of protection measures, a level above which the inconvenience of wearing them prevents them from being used effectively when exposed to hazards or preventing of providing normal operation.

When designing individual protection measures, appropriate protection classes should be considered for foreseeable, differentiated conditions of use in which multiple hazard levels can be identified.

When working with sulfuric acid, the following personal protective equipment is required: goggles and gas mask with absorber according to norm PN-EN-141, acid resistant suit, acid resistant gloves and easily washable shoes.

The characterization of the level of protection is the breakthrough time of the PPE material by chemical substance, also referred to as the period from the beginning of the test to the time when the penetration rate of the test substance reaches 1 $mg \cdot cm^{-2}$ (see table 1).

Table 1. Resistance classes of protective clothing

Resistance class	Breakthrough time [min]
6	>480
5	>240
4	>120
3	>60
2	>30
1	>10

The class 6 of protective clothing is intended for use during sulfuric acid handling.

Measurement of factors harmful to health

The conditions to be fulfilled in the work environment are described in the following Polish regulations:

- Regulation of the Ministry of Health of 30 December 2004 on occupational safety and health related to the presence of chemical agents in the workplace (Dz. 05.11.86)[57], as amended.
- Regulation of the Ministry of Health of 2 February 2011 on the testing and measurement of health hazards in workplace (Journal of acts 2011 nr 33 item 166)[58].

[57] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20050110086
[58] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20110330166

- Regulation of the Ministry of Labour and Social Policy of 6 June 2014 on the maximum permissible concentrations and intensities of agents harmful to health in work environment (Journal of acts 2014 item 817)[59] as amended.

In case of hazardous chemical or dust, the tests and measurements shall be carried out: 1) at least once every two years - if during the last test and measurement concentration of health determinant was greater than 0.1 to 0.5 of the highest permissible concentration (NDS)

2) at least once a year - if during the last examination and measurement the concentration of health determinant was greater than 0.5 value of NDS (Maximum Permissible Concentration - 0,05 mg / m^3).

Comparison of the NDS levels in different EU countries is shown in table 2.

Table 2. Comparison of the highest permissible sulfuric acid (NDS) levels in EU

Country	Limited value – 8 hours working day	Limited value – short working time
	mg/m^3	mg/m^3
EU	0,05 toracalfraction	-
France	0,05 toracalfraction	3
Germany	0,1 inhaling of aerosols	0,1 inhaling of aerosols
Italy	0,05	-
Spain	1	3
Sweden	0,1 dust inhalation	0.2 dust inhalation

Toracal fraction - aerosol fraction penetrating into the chest airways, which poses a health risk after depositing in the tracheobronchial area and the gas exchange area.

Storage

Technical solutions for storage rooms for sulfuric acid

Storage of sulfuric acid in Poland is governed by the Polish Regulation of the Minister of Spatial and Building Industry of 27 January 1994 on health and safety at work using chemicals for water treatment and waste water treatment[60].
Concentrated sulfuric acid storage warehouses should be equipped with natural and mechanical ventilation with enclosure of dust emission to the environment and general ventilation of the room. Suction ventilation openings should be at the working plane or below. On the other hand, general ventilation fans should be located in the upper part of the room and on the floor.
The ventilation performance should be adjusted to the storage room and provide at least 5 exchanges of air per hour and not to exceed the maximum sulfuric acid (NDS)

[59] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20140000817
[60] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU19940210073

concentration at the working place. In Poland, the present value of the highest permissible concentration (S) for sulfuric acid (VI) is 1 mg / m^3 and the maximum permissible concentration of 3 mg / m^3 for sulfuric acid (VI). According to the Scientific Committee (SCOEL) in the European Union and contained in Directive 2009/161 / EC[61], the NDS values for toracal fraction at 0.05 mg / m^3.

Sulfuric acid container should be protected against direct sunlight and heat, and if is stored in building, should be separated from other rooms by permanent building baffles and have flooring made of acid-resistant materials.

In addition, the walls used for storage of sulfuric acid should be painted with acid-resistant enamel. No other materials may be stored in the storage room of sulfuric acid, in particular: nitrate, carbide, cyanide, flammable substances and organic compounds. Therefore, sulfuric acid should only be stored with materials of the same class of danger. In the store, concentrated sulfuric acid should be stored in special stationary tanks. The most commonly used materials for the construction of sulfuric acid tanks are: steel - only when in contact with concentrated sulfuric acid (92 - 98%); Stainless steel; Teflon; Polyethylene - at 20 ° C full range resistance; Polypropylene – at a temperature of 20 °C full range resistance.

Sulfuric acid tanks should be placed on acid-resistant trays, which can fall down during the breakdown of the entire contents of the tank. Collection of sulfuric acid from a container with a capacity not exceeding 60 dm^3 should take place in a separate location, which should be equipped with:

- acid-proof tray, which can hold the contents of the container,
- mechanical ventilation and local exhaust, made of acid-resistant materials,
- installation for safe transfer of fluids,
- acid-resistant sink with running water and pipe fitting,
- acid-resistant internal sewers, equipped with a special tank to neutralize acid.

When collecting concentrated sulfuric acid from steel tanks, the pump should be prevented from penetrating moist air into the tank. Sulfuric acid from the warehouse should be collected in the original factory packaging. Packages (containers) that have been opened must be re-sealed and stored vertically to avoid leakage. Each container in which concentrated sulfuric acid is stored should be properly marked. The storage room where sulfuric acid is stored and collected should be provided with emergency water spray and local extractor.

The storage tank should have a vent from the highest point, because of the possibility of hydrogen accumulation generated during contact with the steel sheet. Tanks should stay on acid resistant floor. Sulfuric acid tanks should be made of materials resistant to this substance such as steel, acid resistant steel, high density polyethylene. The storage area should have an acid resistant floor sloping towards the sewers and an accessible sewer.

Waste management

[61] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:338:0087:0089:PL:PDF

Disposal of waste such as tanks and sulfuric acid residues must be carried out in a safe manner both for man and the environment. Sulfuric acid has a waste code 060101. In Poland, there are legal regulations concerning waste, packaging management and packaging waste recorded in the following acts and the Polish Regulation of the Ministry of Environment:

- Act of 14 December 2012 on waste. (Act Journal 2013, item 21)[62];
- Act of 13 June 2013 on packaging and packaging waste management (Act Journal 2013, item 888)[63];
- Regulation of the Minister of Environment of 9 December 2014 on the waste catalogue (Journal of Laws of 2014, item 1923)[64].

EU regulations are also respected:

- Council Directive 75/442 / EEC on waste - amended and extended by Council Directive 91/156 / EEC, Council Directive 91/692 / EC, Commission Decision 94/3 / EC (European Waste Catalogue), and Decision 96 / 350 / EC[65];
- Commission Decision 76/431 / EEC setting up a Waste Management Committee[66];
- Council Directive 91/689 / EC on hazardous waste, amended by: Council Directive 94/31 / EEC and extended by Council Decision 94/904 establishing the list of hazardous wastes pursuant to Article 1 4 Directives 91/689 / EEC[67].

In addition, used containers should be shipped to specialized companies with appropriate waste management permits.

Environment

Sulfuric acid is also harmful to the environment. It causes carbonization of organic matter and destruction of plant and animal tissues. It is toxic to fish and algae, and after exposure to large quantities of soil or water, it endangers the supply of drinking water. In order to prevent its release, grates and drainage gates must be protected to prevent the acid from entering the sewage and the water.

In the case of a large spillage of sulfuric acid, the leak should be stopped by taking all necessary precautions. To neutralize large amounts of spilled sulfuric acid, cover with non-combustible absorbent material such as sand, earth, vermiculite or diatomaceous earth, and collect into an acid-resistant closable container. Spilled material can also be neutralized with sodium carbonate, sodium bicarbonate or sodium hydroxide. Thoroughly rinse the contaminated surface with water. Contaminated absorbent material may provide the same hazard as a spilled product.

[62] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20130000021
[63] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20130000888
[64] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20140001923
[65] http://eur-lex.europa.eu/legal-content/PL/TXT/?uri=CELEX:31991L0692
[66] http://eur-lex.europa.eu/legal-content/PL/TXT/?uri=CELEX:31976D0431
[67] http://eur-lex.europa.eu/legal-content/PL/TXT/?uri=celex%3A31991L0689

Transport of dangerous goods

Transport of sulfuric acid can be by road, rail or sea, which can be a significant risk of accidents. Therefore, in order to ensure the best security conditions, various types of actions are enacted by state authorities in both national and EU legislation. In Poland, the transport of dangerous goods by road and rail is governed by the following Polish acts:

- The Act on the Carriage of Dangerous Goods Act of 19 August 2011 on the Carriage of Dangerous Goods[68].
- Ordinance of the Minister of Infrastructure and Development of 7 May 2015 on obtaining a certificate of safety adviser for the carriage of dangerous goods[69].
- Regulation of the Minister of Transport, Construction and Maritime Economy of 15 February 2012 on examinations for drivers carrying dangerous goods[70].
- Regulation of the Minister of Transport, Construction and Maritime Economy of 15 February 2012 on the admission certificate for an ADR vehicle[71].
- Regulation of the Minister of Transport, Construction and Maritime Economy of 25 April 2012 on the report on the control of the carriage of dangerous goods by road[72].
- Regulation of the Minister of Transport, Construction and Maritime Economy of 13 April 2012 on transportable pressure equipment[73].

The EU Directives also apply:

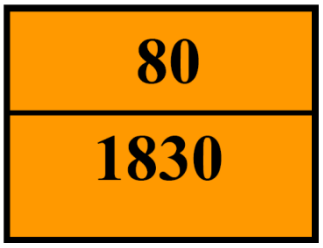
- Council Directive 95/50 / EC of 6 October 1995 on uniform procedures for the control of the transport of dangerous goods by road[74].
- Council Directive 94/55 / EC of 21 November 1994 on the approximation of the laws of the Member States with regard to the transport of dangerous goods by road[75].

In Poland, a coding system is also used in the transport of dangerous goods. For road transport ADR system is used, while for rail transport it is RID. ADR is an international convention for the carriage of goods and dangerous goods by road. This system is applicable almost throughout Europe and it is also in Poland.

[68] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20112271367
[69] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20150000718
[70] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20120000191
[71] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20120000192
[72] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20120000483
[73] http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20120000436
[74] http://eur-lex.europa.eu/legal-content/PL/TXT/?uri=CELEX%3A31995L0050
[75] https://publications.europa.eu/pl/publication-detail/-/publication/0712a57f-f67e-41ea-be5b-84ff8a6aeecb/language-pl

ADR/RID provide signs of means of transport of hazardous materials with orange warning signs measuring 30 x 40 cm, reflective orange around the black non-reflective strip.

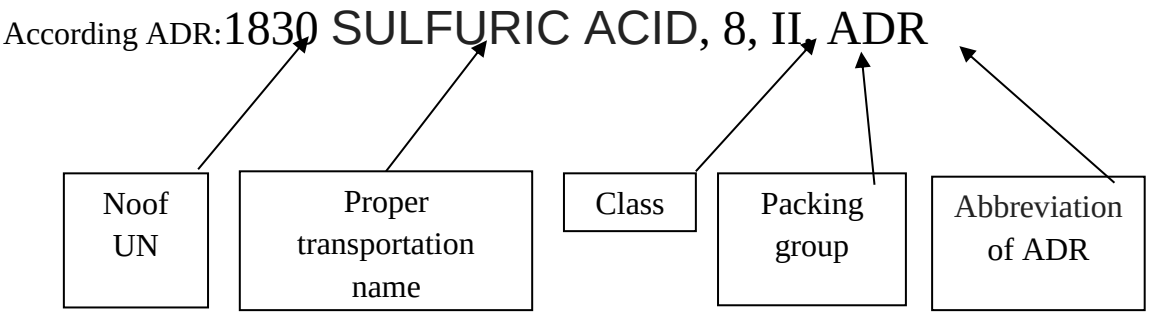
Each of the most dangerous materials has been given two relevant identification numbers, i.e. the hazard identification number consisting of two or three digits and the distinguishing number of the material (according to the catalogue) consisting of four digits.



80 - Corrosive or slightly corrosive material.

1830 Concentrated sulfuric acid.

In contrast, each tanker carrying sulfuric acid should be labelled according to ADR as follows:



In addition, the transport should bear the pictogram:

In the case of transport of hazardous materials by rail in Poland, the Regulations for International Carriage of Dangerous Goods are in force. Rail tank designation is the same as for wheeled transport. Maritime transport of dangerous goods is based on the IMDG Code - the International Maritime Dangerous Goods Code, whose recommendations are not introduced directly into Polish law. In order to reduce the risk of danger and thus increase security, Poland has signed the following agreement for this purpose:

ADN – European Agreement concerning the International Carriage of Inland Waterways of Dangerous Goods (ADN), signed in Geneva on 26 May 2000 (Journal of Laws of 2010, No. 235, item 1537)[76], as amended from the date of entry in relation to the Republic of Poland.

Examples – Scenarios for Poland

"In storage" slurry acidification system

Under Polish conditions it is envisaged that this method of acidification of slurry with sulfuric acid will be appreciated among farmers for economic reasons and simple construction. This is justified since an external tank is used in nearly every farm for slurry storage.

Sulfuric acid (96%) is used to acidify slurry in the tank. The entire system for acidifying slurry in a concrete tank (in storage) is mounted on an agricultural tractor (Fig.13), and driven from the tractor PTO.

Fig. 13. A system for acidifying slurry in a tank mounted on a tractor.

The system includes a stirrer at the end where the acid dispensing nozzle is located, the slurry pump and the entire piping system with a check valve and an acid dosing pump. Sulfuric acid is stored in a pallet made of plastic, placed directly at the side of

[76]http://prawo.sejm.gov.pl/isap.nsf/DocDetails.xsp?id=WDU20102351537

the slurry tank. The principle of operation of the system consists in starting the pump, which results in the formation of a vacuum in the suction nozzle. The pump sucks raw slurry from the top of the tank, but through the nozzle flows the acid sucked through a pipe immersed in an acid-laden pallet, which is then dosed and mixed with slurry in a concrete tank.

To control the pH level of slurry, a pH meter is mounted in the tank. When sulfuric acid is dispensed into the slurry, a chemical reaction occurs, resulting in a high amount of foam. Therefore, it is important to pay special attention to the tank where the slurry is filled up to 2/3 of its volume. Foam together with acidified slurry will float on the surface of the tank. If too much foam is released, the acid dosage is discontinued until it is dropped. Continuing the mixing of acidified slurry causes the pH of slurry to decrease in proportion to the amount of sulfuric acid added. The separated foam consists of viscous micro bubbles which are resistant to cracking.

This also has its advantages, namely it prevents the smell of slurry and the release of nitrogen into the atmosphere during mixing. The pH value of acidified slurry depends on the length of time of slurry storage in the tank. If acidified slurry is stored long in the tank, its pH will increase. Therefore, the slurry acidified in tank should have a pH value of 5.5-6 just before application to the field. The whole process of acidifying slurry in the tank should be carried out with all security measures. Therefore, an operator working on acidification of slurry should be provided with specialist protective clothing (overalls) with a special respiratory protection mask against sulfuric acid vapours. To increase the safety of acidification of slurry in the "in storage" system, there is also a water tank in the tractor, in case of an accident, to rinse the acid-scavenged surfaces.

Upon completion of the acidification, the entire system is rinsed with a mixture of water and compressed air, while the empty paleto-container after acid passed to the supplier or if necessary replaced to full. The advantage of using this system is the localization of acid and slurry in one place and the mobile device mounted on the tractor can serve to acidify slurry in more tanks in a short time.

Remarks:

1. Bearing in mind that the SAT method has not been widely used in Poland yet, in case of doubt, the solutions used in Sweden and Denmark should be followed.
2. Check the validity of legal provisions.

Sweden

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General aspects

Laws and regulations change over time. Always check with national and local authorities, such as Länsstyrelsen, MSB, Arbetsmiljöverket and Naturvårdsverket for up-to-date regulations. An overview of Swedish legalisations is presented in Annex Table 1.

Personal safety

Is permission required?

In accordance with the Swedish Chemicals Agency's Ordinance (2008:245) and Chemical Products and Biotechnical Organisms Regulations (2008:2), sulphuric acid used within a business company does not require a permit, in accordance with the regulations on permits for particularly dangerous chemicals. Neither are permits or notification required under the Swedish Environmental Regulation (2013:251) for using or storing sulphuric acid, provided it is managed professionally. However, a permit is required by private individuals handling it and by those who transfer (e.g. sell) the product in the course of business.

In Sweden, sulphuric acid may be transferred to persons for their use for professional purposes only if they have a permit for its handling or handle it under certain exceptions. It is essential that persons using the acid for professional purposes are informed about its hazards through Safety Data Sheets and the hazard labelling on the packaging. The labelling must include hazard pictograms, signal words and the hazard class and safety statements in accordance with CLP.

Legalisation of occupational safety and health

The Swedish Work Environment Authority's provisions state that the employer is responsible for determining how ill health and accidents caused by chemical hazards at work are to be prevented. This is also valid for persons without employee's accordance with the Work Environment Act[77], when running activities where ill health may arise, but exempt from the information requirement. Persons supplying contract workers must ensure that the workers supplied do not commence work before checking, through their customer's documentation, that an investigation and risk assessment have been carried out and the necessary risk-limitation measures have been taken. Accordingly, no work may commence before an investigation and risk assessment and any necessary measures have been implemented. In accordance with the provisions, there are obligations to inform about the risks and to keep this documentation available. There is also a checklist to use as a basis for information.

The risk of chemical hazards causing ill health or accidents in the activity must be investigated and assessed as often as the activity necessitates. In accordance with the

[77] Work Environment Act (1977:1160) Chapter 3, section 5.

Work Environment Ordinance[78], the employer's work environment management system must ensure compliance with certain specified REACH requirements in the activity. Work may not commence before an investigation and risk assessment have been carried out and the necessary measures taken to prevent potential ill health and accidents at work. The purpose of the provisions is to determine how ill health and accidents caused by chemical hazards at work are to be prevented.

In accordance with the Swedish Work Environment Authority's provisions[79] and general guidelines, the employer must consult with employees on what health risks there may be, and where; how these can be avoided/rectified; who is responsible for rectification; and by when the rectification must be completed. The review must be documented, and dated and signed by the person carrying out the survey. The persons and the parts of the activity that participated in the risk assessment must be named. The risks must be reviewed and assessed as often as the activity necessitates, for example in the event of temporary or permanent changes or if new information could affect the risk assessment. The list must record:

- The type of hazard
- Where it is stored, and where it is used
- Any occupational exposure limit values
- Other special rules that may apply

Safety data sheets and other information about risks and protective measures must be available in the activity. The supplier is obliged to provide these.

Exposure limit values in Sweden

There are mandatory limit values on how much sulphuric acid may be present in the air. The Swedish Work Environment Authority's provisions[80] on occupational exposure limit values have recently been amended to correspond better to the EU's indicative[81] limit values stated in various directives. If an employee is exposed to several types of air pollutants, the following Work Environment Authority provisions apply concurrently: Occupational exposure limit values and Chemical Hazards in the Working Environment (plus Microbiological Work Environment Risks – Infection, Toxigenic Effects, Hypersensitivity, not relevant in this instance).

In accordance with the Swedish occupational exposure limit values for inhalable sulphuric acid, air may contain a maximum of 0.1 mg /m^3 in accordance with the threshold limit value (TLV) and 0.2 mg/m^3 in accordance with the short-term limit value (STEL). The short-term limit value is intended as a guide, which means the threshold is to be used as a recommended maximum value that should not be exceeded. For sulphuric acid, the short-term exposure limit value relates to a reference period of 15 minutes. Sulphuric acid is also classified as carcinogenic (C).

[78] 12 a § in the Work Environment Ordinance (1977:1166).
[79] The Swedish Work Environment Authority's provisions and general guidelines (AFS 2011:19) on chemical hazards in the working environment.
[80] AFS 2015:7 The Swedish Work Environment Authority's provisions and general guidelines on occupational exposure limit values.
[81] Directive 2006/15/EC Indicative Occupational Exposure Limit Values.

It is therefore essential to wear the correct personal protective equipment whenever handling it. The safety data sheet specifies measures such as respiratory, eye, face, hands and skin protection. This involves the correct kinds both of acid-resistant materials and of fully covering/tight-fitting protection/clothing.

The Swedish Work Environment Authority's provisions state that the employer is responsible for compliance with occupational exposure limit values. This is also the case for persons running activities without employees, in accordance with the Working Environment Act. Persons that take on contract workers are placed on an equal footing with employers. This responsibility also falls on persons controlling a work place.

The Work Environment Act includes regulations concerning the obligations of employers, and others responsible for safety, to prevent ill health and accidents at work. There are also regulations about the cooperation between employer and employee, for example regarding the safety representative's activities.

List of legalisations of occupational safety and health

Work Environment Act (1977:1160)

The Work Environment Ordinance includes among other things regulations concerning employer responsibilities to report work-related injuries and to appoint a safety representative.

Work Environment Ordinance (1977:1166)

There are also provisions and guidelines concerning exposure limit values that applies to all workplaces with existing air pollutants.

AFS 2015:7 The Swedish Work Environment Authority's provisions and general guidelines on occupational exposure limit values.

The below provisions include regulations concerning risk assessment, requirements for the provision of safety data sheets, labelling of chemical hazards, etc.

Chemical Hazards in the Working Environment Hazards (AFS 2011:19) provisions. Amended and reprinted in AFS 2014:43

Storage

The product must be stored in such a way that prevents health and environmental risks in accordance with the Swedish Work Environment Authority and the Environmental Code. Sulphuric acid is a highly corrosive chemical that must be stored under lock and key unless it is kept under supervision. The requirement is the same if the acid is stored in the field: under lock and key or under supervision. Compare with the requirements for class 1L plant protection products.

Environment

The Swedish Environmental Code's[82] ordinance on serious environmental damage[83] regulates discharges to soil and water. One of the Environmental Code's objectives is to protect human health and the environment against damage and disturbance whether caused by pollution or some other effect. Applying this to the handling of the sulphuric acid means discharges to waste-, ground- and surface water must be prevented. Spillages are confined and absorbed, using absorbent material, sand, diatomaceous earth or similar, and collected. Sawdust, bark or similar materials must not be used because of the risk of fire. The contaminated area is sluiced with water. Major spillages are dammed in suitable receptacles, and the emergency services are contacted. If necessary, buffering lime or sodium carbonate is applied. It is important to have buffering material available during handling. Waste from the clean-up is dealt with as dangerous waste. Major discharges to the wastewater system may harm the wastewater treatment plant by inhibition of the sludge or biofilm organisms due to acidification.

Waste classification

Sulphuric acid residues (more than 1% of the container volume) are considered dangerous waste and must be handled accordingly. It must be stored and transported in shockproof, sealed and clearly labelled containers. The waste code is 06 01 01*, which is recorded[84] in the dangerous waste logbook that must be available in every activity. The container itself is regarded as dangerous waste (code 15 01 10*) if it contains residues of or is contaminated by sulphuric acid. Waste codes are listed in the European Waste Catalogue (EWC).

Transport of dangerous goods

Transport or handling of dangerous goods is subject to many laws, such as those for the work environment, the environment, chemical products and biotechnical organisms, waste, regulations for water protection areas, local traffic regulations, flammable and explosive goods and protection against accidents. ADR, European Agreement concerning the International Carriage of Dangerous Goods by Road, ensures consistency between all these regulations in European countries. The Swedish version of ADR is named ADR-S[85].

According to the Swedish Civil Contingencies Agency (MSB[86]), dangerous goods[87] are substances and articles that, because of their chemical or physical properties, can cause damage to life, health, the environment or property during transportation. For

[82]Environmental Code 1998:808 Chapter 2 and Chapter 10.

[83]Ordinance (2007:667) on serious environmental damage.

[84]Waste Ordinance SFS 2011:927. Professional activity giving rise to dangerous waste: record in chronological order 1. Annual quantity produced, and 2. to whom the waste is handed over for further handling. Keep for at least three years.

[85]https://www.msb.se/sv/Forebyggande/Transport-av-farligt-gods/Lag-forordning-och-foreskrifter/MSBs-foreskrifter/ADR-S/

[86]Information brochure (in Swedish): Transport av farligt gods.Väg och järnväg 2015/2016. Publ.no: MSB805 – March 2015. ISBN: 978-91-7383-531-2.

[87] Dangerous goods are regulated in the Transport of Dangerous Goods Act (2006:263), Transport of Dangerous Good Ordinance (2006:311) and Regulations on the transport of dangerous goods by road, rail, sea and air.

example, dangerous goods may be explosive, flammable, toxic, radioactive or corrosive. Examples of dangerous goods include petrol, diesel, liquefied petroleum gas, cigarette lighters, sulphuric acid, arsenic, fireworks, aerosol cans, airbags, smoke detectors and water pollutants.

ADR driver training certificate

Sulphuric acid is classified as dangerous goods, so ADR training is required to be permitted to transport it. In Sweden, MSB is responsible for training and examining drivers and issuing ADR certificates[88].

Exemptions related to quantities carried per transport unit

One way to transport dangerous goods with some relief from the regulations in ADR is to use the rules on *exemptions related to quantities carried per transport unit* [89]. The method can be used when the transfer takes place only within an area where dangerous goods are manufactured, stored or used.

Sulphuric acid is in transport Class 2. The total quantity of acid transported is therefore to be multiplied by a factor of 3 in accordance with the table. For sulphuric acid, the result value must be max. 1000, to allow transportation under this exemption. The calculations show that a maximum of 333 litres[90] of sulphuric acid may be transported under the exemptions of quantities carried per transport unit. The driver only needs 1.3 training. The load must be in a labelled type-approved container carrying the symbol:

The goods declaration must accompany the load. The vehicle must be equipped with at least one fire extinguisher with a minimum capacity of 2 kg dry powder. The load must be secured, and regulations covering how it is loaded, unloaded and handled must be available.

The goods declaration must include information on the total and calculated quantities. For 96% sulphuric acid, this could be:

UN 1830 Sulphuric acid, 8, II, Corrosive Transport class 2: 333 litres (value 999).

Limited quantity

In this instance, the sulphuric acid must be packed in max. 1 litre containers and in cardboard boxes to max. 30 kg per package (including the weight of the packaging). The total weight of all the packages must not exceed 8 tonnes. This requires 1.3 training. Since each movement is less than 8 tonnes, the vehicle need not carry

[88] https://www.msb.se/en/Prevention/Transport-of-dangerous-goods/Training-/
[89] ADR, Annex A, chapter 1.1.3.6
[90] The value is below 1000, i.e. 333 litres multiplied by 3 = 999.

dangerous goods symbols. However, the packages must be labelled with the symbol shown below, and with directional arrows because a liquid is being carried.

This exemption is unpractical to apply on acidification of slurry on a farm because of the limitation on max. 1 litre packages (fig. 14).

Fig. 14. Example of goods for transportation with limited quantity of liquid. From MSB, Transport av farligt gods, Väg och järnväg 2015/2016.Publ.no: MSB805 – March 2015, ISBN: 978-91-7383-531-2 (in Swedish).

Education '1.3 training'

The transportation of dangerous goods under certain exemptions and reliefs, such as *exemptions related to quantities carried per transport unit*, limited and reduced quantities, does not require driver training with an ADR certificate. However, the requirements of what is known as 1.3 training must be met. In addition to transportation, the training requirement also applies to persons that (for example) pack, load or unload dangerous goods, and to others whose tasks relate to the transport of dangerous goods, in this instance by road.

The purpose of the training is to educate personnel about the risks and dangers associated with the dangerous goods, and the applicable regulations. Certificates are issued by those providing the training, not MSB. A detailed description of all completed training, including refresher courses, must be retained by the employer for at least five years, and be made available upon request by the employee or the authority responsible. Training documentation must be verified when a new employment begins. For example, the documentation may consist of the employer having training records and the employee having a certificate. If a person is to perform tasks they are not trained for, this may only be done under the supervision of a trained person. The training has three parts (relating to sulphuric acid): **General Awareness Training** in the provisions for the carriage of dangerous goods; **Task-specific training** in the provisions commensurate with the duties and responsibilities of the personnel; and **Safety training** in the hazards and dangers that dangerous goods can present in the activities of the personnel during transportation, loading and unloading.

Training is repeated every two years to take account of changes to the regulations, which occur at the same frequency. The employer must retain a detailed description of the training for five years. The MSB website has information on the locations of ADR trainers (who also train in 1.3).

Safety adviser

The obligation in accordance with MSB to have a safety adviser applies to those who transport or hand over dangerous goods for transportation. Transport is defined as "the movement of dangerous goods by means of transport, and such loading, unloading or handling that forms part of the movement"[91]. All those directly involved in the transport of dangerous goods must have an adviser, as must both consignors and carriers. Nevertheless, there are exemptions for the transportation of value calculated or limited quantities. However, having a safety adviser for discussing regulations and precautionary measures is recommended. As an example, Swedish MSB has a list of authorized safety advisers in the country.

Examples – Scenarios for Sweden (based on five existing techniques to acidify slurry)

Basic conditions

In all the scenarios described below, the Work Environment Ordinance[92] requires the employer (the farmer or contractor manager), before starting to handle sulphuric acid, to carry out an investigation and risk assessment and to take the necessary measures to prevent any ill health and accidents at work (systematic work environment management). In the various scenarios, the term farmer also includes employees or contract labour. However, contractors (with or without employees) have their own employer responsibility since contractors are retained to carry out the entire job from start to finish. In this case, the farmer hands all handling of sulphuric acid over to the contractor. It is essential that the contractor has access to safety data sheet, and that there is consultation with the farmer on safety risks and safety measures. Before work with acid commences, persons supplying contract labour must ensure (via the customer's documentation) that an investigation and risk assessment have been carried out and the necessary risk limitation measures taken. Sometimes it can be difficult to determine whether the work is being carried out by contracted labour or under a contract. Guidance is available in a table in the Swedish Work Environment Authority's publication H432[93] (in Swedish).
Handling of acids mainly covers sulphuric acid with a concentration of at least 96% or, as in the case of Scenario 5 Kyndestoft, the use of 50% sulphuric acid. According to the Swedish Chemicals Inspectorate's regulations on chemical products, sulphuric acid used for professional purposes in the business does **not** require a permit in accordance with the regulations on permits for particularly dangerous chemicals. Necessary protective equipment/emergency showers/eye wash showers must be available, as well as other protective measures to rectify any spillages to land, groundwater and surface water. Safety data sheets must be available and strictly complied with. **No one under 18 years old** is permitted to handle sulphuric acid for professional purposes.

The examples are based on the use of 2 litres sulphuric acid per m^3 manure in storage and of 1 litre sulphuric acid per m^3 manure mixed into the slurry at the time of

[91] https://www.msb.se/sv/Forebyggande/Transport-av-farligt-gods/Sakerhetsradgivare/ (in Swedish)
[92] Work Environment Ordinance 1977: 1166, 12 a §.
[93] H432 Arbetsmiljöansvar – *för personal som är inhyrd eller arbetar på tillfälliga arbetsplatser, page 21 (in Swedish). Swedish Work Environment Authority 2008.*

application in the field. The spreader's tank capacity is 25 m^3. The volume of slurry to be handled is assumed to be 3000 m^3. The sulphuric acid consumed is 3000 litres (3 m^3) or 6000 litres (6 m^3). The vendor/supplier/carrier of the sulphuric acid is/are approved for transportation to the farm.

The precautionary measures are summarized as follows:

Safety in use

- Keep people and animals well away from the sulphuric acid when it is being handled by trained personnel.
- Sulphuric acid must not be stored/handled above head height.
- Keep plenty of water on standby and in the form of a shower (Fig. 5) and eye wash showers.
- Ensure you know how sulphuric acid reacts with slurry and water (e.g. violent foaming).
- It is essential to have first aid knowledge and to know the location of protective equipment on the farm.
- All serious accidents[94] and serious incidents must be reported to the Swedish Work Environment Authority.
- Appropriate personal protective equipment is acid-resistant safety boots/shoes; fully covering acid-resistant protective suit (e.g. in butyl rubber or neoprene), which may be disposable; protective gloves (e.g. in fluorocarbon rubber or butyl rubber); protective eyewear or a full-face mask (with gas filter E, release of sulphur dioxide, or an aerosol mask with filter P3, mist formation) in accordance with SS-EN 141. See above under the heading Protective equipment, training, and Fig. 1 and 2.
- Have buffering material available in case of spillage.
- Follow the manufacturer's recommendations.

Scenario 1 - with technology from JH AgroA/S

The farmer buys acidification technology from JH Agro for acidification either for slurry in the livestock barn or in storage. The acid is mixed with manure in a mixing container outside the animal housing. Dosing and mixing of acid in the manure are automatic. Following acidification, the acidified manure is pumped either back into the animal housing or into the storage container. The acid storage tank is located outside the animal housing and near a mixing container. A safe storage tank for sulphuric acid is included in JH Agro's equipment, along with other equipment such as pumps, pH meter, control system, emergency shower and eye wash shower. The acid tank is dimensioned to be sufficient for 6-12 months.

The farmer orders sulphuric acid from an authorized dealer, who transports the acid to the farm in a truck/tanker. The dealer is also responsible for filling the storage tank with acid. The farmer then transports the acidified manure to field for application. In this scenario, the farmer never actually handles the acid.

[94]In 3 Chapter 3a § of the Work Environment Act, the notification requirements are limited to accidents resulting in death or severe personal injury or that affect multiple employees simultaneously.

Dangerous goods or not?

Acidified manure containing 2 litres sulphuric acid per cubic metre slurry (a 0.2% solution) is not classified as corrosive. Transportation for application in the field is **not regarded as being of dangerous goods** and therefore requires no special safety measures.

Scenario 2 - with technology from HarsøMaskiner A/S

The farmer buys technology from HarsøMaskiner for acidification in the storage facility or the technology is owned by a contractor, who is hired for doing the mixing and acidification. This system is based on an injector agitator. When the equipment is used, the manure is agitated while sulphuric acid is sucked from a 1000 litre (1 m^3) IBC. The container is positioned alongside the tractor driving the injector agitator. IBCs containing 96% sulphuric acid are delivered to (or existing IBCs are filled on) the farm by an authorized dealer. The farmer will almost certainly have to move the IBC by tractor from the delivery point to the storage tank near the agitator six times during acidification. Given a flow rate of 100 litres sulphuric acid per minute, it takes about 10 minutes to empty an IBC. The farmer is responsible for the acidification, which can take 1-3 hours depending on the amount of manure to be treated and how much foam is formed. It is the farmer that connects the line between the injector agitator and the IBC, measures pH and changes IBCs during acidification. The farmer must wear full personal protective equipment throughout the acidification process. It is strongly recommended that everyone using sulphuric acid for professional purposes should have completed a course on how to handle sulphur acids safely.

Dangerous goods or not?

Usually, the farmers moving IBCs containing 1 m^3 sulphuric acid, must have undergone driver training and hold an ADR certificate. However, in Sweden transporting sulphuric acid in IBCs with tractors is an exception from required ADR-training.

The acidified slurry with pH of 5 to 6 in the tanker is not corrosive and is **therefore not classified as dangerous goods**.

Scenario 3 – with technology from Ørum-Smeden

The farmer buys acidification technology from Ørum for acidification in the storage facility or the technology is owned by a contractor, hired for mixing and acidification. This system is based on a propeller agitator with nozzle system, in connection with an acid delivery tanker. When the agitator is used, the acid is pumped from the truck tanker, that delivers the acid to the farm, through the nozzels directly into the slurry storage. In the Danish experience of acidification in a storage facility, 2 litres of sulphuric acid per m^3 slurry is used (SEGES, 2015). The sulphuric acid is ordered from an authorized dealer. The truck driver, who has driver training with an ADR certificate for handling sulphuric acid, takes care of connecting the line between the tanker and the agitator and pumping the acid. The farmer is only responsible for agitation and pH measurement in the manure storage tank. Once acidification is complete, the tanker leaves the farm.

Dangerous goods or not?

The farmer or contractor do not transport, move or handle the sulphuric acid as it is done by the authorized dealer. Transportation of acidified slurry is **not regarded as**

being of dangerous goods and therefore requires no special safety measures when transported to the field.

Scenario 4 – with technology from Biocover A/S

The farmer buys acidification technology from Biocover for acidification directly in the field or hire a contractor to do the work. In this instance, it is assumed that 1 litre acid is used per cubic metre slurry (SEGES, 2015). When this system is used, sulphuric acid and slurry are mixed in the fields during the application phase. The sulphuric acid is transported in an IBC on the front of the tractor in a strong steel safety basket. The acid is mixed into the slurry at the very back of the slurry tanker immediately before the slurry goes to the spreader. The safety basket carries a powder fire extinguisher, a water tank and an eye wash. The farmer buys three 1-m^3 IBCs approved for sulphuric acid, and arranges with an authorized dealer to have them filled. The sulphuric acid is delivered to the farm by tanker. The truck driver, who has driver training and an ADR certificate, is responsible for filling the empty IBCs. The IBCs are put in the safety basket using the front lift on the tractor. Cameras are mounted on both the front and side of the basket to facilitate loading and driving. The line from the IBC to the tanker on the tractor is connected using a manually quick coupling, so the farmer need never come into contact with the sulphuric acid. After filling, the farmer transports the acid from farm to field in the front-mounted safety basket. Following application, any acid left in the IBC is driven back to the farm in the same way. The IBC can then be unloaded at the storage site. Disconnecting, unloading, loading and hitching are expected to take about 3 minutes.

The farmer should at least wear protective eyewear and protective gloves when opening and closing the safety basket and when connecting the line between IBC and tractor tanker. It is strongly recommended that everyone using sulphuric acid for professional purposes should have completed a course on how to handle it safely.

Dangerous goods or not?

Usually, the farmers moving IBCs containing 1 m^3 sulphuric acid must have undergone driver training and hold an ADR certificate. However, in Sweden transporting sulphuric acid in IBCs with tractors is an exception from required ADR-training.

Scenario 5 - with technology from KyndestoftMaskinfabrikApS

The farmer buys acidification technology from KyndestoftMaskinfabrik for acidification in the field or hires a contractor with the technology to do the acidification. When this system is used, sulphuric acid and slurry are mixed in the field during the application phase. This system uses 50% acid, which doubles the quantity of acid required to reach the desired pH (SEGES, 2015). The Kyndestoft equipment is available in three different size containers (1000, 1500 and 2000 litres). If a 1500 litre tank is used, it will have to be filled four times to empty the slurry storage tank, assuming a dosing rate of 3 litres per cubic meter of slurry. The acid container for the Kyndestoft system is a purpose-made reinforced plastic and fibreglass container with an outer steel crash cage which mounted on the front lift of the tractor. The acid is mixed into the slurry flow at the very back of the slurry tanker immediately before the slurry goes to the spreader.

The sulphuric acid is stored on the farm in either a fixed storage tank approved for the purpose of storing acid, as with the In-house system, or in separate IBC-tanks. The farmer orders sulphuric acid (50%) from an authorized dealer. The dealer transports the acid to the farm in a truck/tanker and is also responsible for filling the storage tank. When filling the container of the Kyndestoft system, the pump of the acidification system is used. The farmer must manually connect the pump from the tractor container to the acid storage. Containers and tanks must be controlled and approved before used for transporting dangerous goods. This control of the tractor container is made before the first time of use, and the control will be repeated regularly during use. The control should be made by a certificated authority for doing such tests.

The farmer must wear full personal protective equipment when filling the tractor mounted container. It is strongly recommended that everyone using sulphuric acid for professional purposes should have completed a course on how to handle it safely.
The farmer transports the acid in the tractor-mounted container from farm to field for application. Following application, any acid left in the container is driven back to the farm and then pumped back to the acid storage tank until the next application.
According to the manufacturer, there is no need for cleaning the system after use.

Dangerous goods or not?

The farmer wants to mix acid with the slurry directly in the field, and transports the acid there in the farmer's container. Sulphuric acid is classified as dangerous goods, so **ADR training is required** to be permitted to transport it and the driver needs an ADR driver training certificate. No exception is given from ADR-training for tractor transport with the Kyndestoft's system as a container is used and not IBC-tanks.

Scenario 6 – the farmer gets himself sulphuric acid

The farmer wishes to use a vehicle and trailer to collect the sulphuric acid from the dealer. For the farmer, this scenario is not feasible in practice because of the large quantities of sulphuric acid to be transported and handled, as well as the major risks to health and the environment that may arise between the purchase and the farm. Neither is this possible in Denmark because suppliers do not allow this transport.

Annex Table 1. Swedish regulations

Work regulations
Work Environment Ordinance (1977:1166)
AFS 2015:7 The Swedish Work Environment Authority's provisions and general guidelines on occupational exposure limit values
Chemical Hazards in the Working Environment Hazards (AFS 2011:19) provisions. Amended and reprinted in AFS 2014:43
The Swedish Work Environment Authority Chemical Hazards in the Working Environment AFS 2011:19, concerning carcinogenic, mutagenic and reproductively toxic substanceshttps://www.av.se/en/work-environment-work-and-inspections/publications/foreskrifter/kemiska-arbetsmiljorisker-afs-201443-provisions/.
Environment protection
Environmental Code 1998:808
Waste
Waste Ordinance SFS 2011:927
Transport
ADR-S, the Swedish Civil Contingencies Agency's provisions on the on- and off-road transport of dangerous goods, MSBFS 2015:1

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Appendix 1. EU regulations

Chemicals
CLP regulation Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures, amending and repealing. Directives 67/548/EEC and 1999/45/EC, and amending Regulation (EC) No 1907/2006.CLP.
Work regulations
Council directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC)
Directive 2004/37/EC of the European Parliament and of the Council of 29 April 2004on the protection of workers from the risks related to exposure to carcinogens or mutagens at work (Sixth individual Directive within the meaning of Article 16(1) of Council Directive 89/391/EEC)
Council directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work (fourteenth individual Directive within the meaning of Article 16(1) of Directive 89/391/EEC).
Environment protection
Directive 2004/35/CE of the European parliament and of the council of 21 April 2004 on environmental liability with regard to the prevention and remedying of environmental damage.
Waste
Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives.
Commission decision of 3 May 2000 replacing Decision 94/3/EC establishing a list of wastes pursuant to Article 1(a) of Council Directive 75/442/EEC on waste and Council Decision 94/904/EC establishing a list of hazardous wastes pursuant to Article 1(4) of Council Directive 91/689/EEC on hazardous waste.
Transport
Directive 2008/68/EC of the European parliament and of the council of 24 September 2008 on the inland transport of dangerous goods.
European Agreement concerning the International Carriage of Dangerous Goods by Road. ADR applicable as from 1 January 2013. UNECE.

Appendix 2: Guidelines and recommendations

- Find a safety advisor
- Make a risk analysis
- Chose the safest technology (no or little risk of contact acid handling)
- Get training
- Follow maintenance program from supplier
- Use protection equipment
- Be prepared for accidents and know what to do

Appendix 3. Checklist for acidification of slurry

The checklist can be used to check that the correct equipment is procured and that recommendations and legal requirements are complied with (Swedish conditions).

Check item	*YES*	*NO*	*Comments/action*
Working environment			
Acid is not handled by anyone under 18			
Risk assessment is completed			
Risk assessment has recorded: 1. Type of hazard 2. Locations of storage and use 3. Any occupational exposure limit values 4. Other special regulations that may apply			
All serious accidents and serious incidents are reported to the Swedish Work Environment Authority.			
Storage of acid			
Acid storage containers are made of a resistant material			
Acid storage is bunded			
Impact protection is provided where there is a risk of collision			
Storage location is chosen with regard to the distance to drinking water supply, nearby watercourses or other risk objects			
Acid is listed in the company's chemical inventory			
Acid is stored under supervision, or under lock and key and inaccessible to children or other unauthorized persons			
Equipment for neutralizing and collecting spillages is easily accessible			

Check item	*YES*	*NO*	*Comments/action*
Check item	*YES*	*NO*	*Comments/action*
Handling			
Safety data sheets are easily accessible wherever acid is handled			
Equipment for neutralizing and collecting spillages is easily accessible			
People and animals are kept well away from sulphuric acid during its handling by trained personnel			
Sulphuric acid is **not** stored/handled above eye level.			
Personnel are fully aware of how sulphuric acid reacts with manure and water, for example the acid-into-water (AIW) rule and violent foaming.			
Knowledge of first aid and where the farm's protective equipment is kept is essential.			
Accidents or major spillages are reported to the municipal environmental and health protection administration and, if necessary, the emergency services.			
Protective equipment			
Protective equipment to be available when handling the acid: 1. Emergency shower, 2. Eye wash shower, 3. Respiratory protection, 4. Protective eyewear 5. Protective gloves in, for example, fluorocarbon rubber or butyl rubber, 6. Fully covering protective suit in, for example, butyl rubber or neoprene (may be disposable) 7. Acid-resistant safety boots/shoe			
Full-face mask with gas filter E to be worn when sulphur dioxide is released, or an aerosol mask with			

Check item	YES	NO	Comments/action
filter P3 when mist is formed, in accordance with SS-EN 141.			

Check item	YES	NO	Comments/action
Transport			
ADR training for transport (excluding transport of IBCs by tractor for agricultural use).			
1.3 training for transport of max. 333 litres (applicable to personnel that for example pack, load or unload dangerous goods, and to others whose tasks relate to the transport of dangerous goods).			
For the transport of value-calculated quantities, the following ADR-S provisions apply: • Personnel, including the driver, have undergone 1.3 training • Packaging, IBCs and bulk packages carry prescribed marking and labelling • Goods declaration is prepared for dangerous goods, with the addition of the value-calculated quantity • Packaging, IBCs and bulk packages are type-approved • Vehicle equipped with at least one fire extinguisher with a minimum capacity of 2 kg dry powder • Goods are grouped in accordance with the provisions of Chapter 7.5 in Part 7. • Load security and loading, unloading and handling are in accordance with the provisions in Part 7.			
Transport training is documented			
Employer retains a detailed description of the training for five years.			

Check item	YES	NO	Comments/action
Supplier's recommendations complied with.			
Safety adviser has been consulted.			

Check item	YES	NO	Comments/action
Waste			
Containers and packages that are not completely clean are handled as hazardous waste.			
Hazardous waste is stored bunded, protected from precipitation and inaccessible to unauthorized persons.			
Waste is transferred to an authorized carrier.			
For self-transported hazardous waste, notification (less than 100 litres/100 kg) or a permit application has been made to the county administrative board			
Transport documentation for transferred waste is prepared and kept for at least three years.			
Records are kept for transferred waste and kept for at least three years.			

Interreg Baltic Sea Region

Baltic Slurry Acidification

EUROPEAN REGIONAL DEVELOPMENT FUND

EUROPEAN UNION

www.balticslurry.eu

Summary of the project

Baltic Slurry Acidification is an agro-environmental project financed by Interreg Baltic Sea Region under the priority area Natural resources and specific objective Clear Waters. The aim of the project is to reduce nitrogen losses from livestock production by promoting the use of slurry acidification techniques in the Baltic Sea Region and thus to mitigate eutrophication of the Baltic Sea. Baltic Slurry Acidification project started on March 2016 and will continue until February 2019.

Summary of the report

This report concerns working environment and safety when implementing technology for acidification of animal slurry in the Baltic Sea Region. Acids, especially sulphuric acid, can be dangerous chemicals. There are several EU regulations governing the sale of chemicals on the market and hazard classification and labelling. Country chapters' present national regulations and key aspects on working environment, personal safety, safe storage and transport. There are also example scenarios for each country describing routines and considerations for safe acid handling when using currently available slurry acidification technologies in that particular country.

Contributing partners

- **Organe Institute Aps, Denmark**
- **Estonian Crop Research Institute, Estonia**
- **Association of ProAgria Centres, Finland**
- **Christian-Albrechts-Universität zu Kiel, Germany**
- **Latvian Rural Advisory and Training Center, Latvia**
- **Lithuanian University of Health Sciences, Lithuania**
- **ITP – Institute of Technology and Life Sciences, Poland**
- **The Rural Economy and Agricultural Society, Sweden**
- **RISE – Agrifood and Bioscience, Sweden**